

Synthetic utility of metal catalyzed hydrogen peroxide oxidation of C-H, C-C and C=C bonds in alkanes, arenes and alkenes: Recent advances

Halina Wójtowicz-Młochowska

Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland

E-mail: halina.wojtowicz@pwr.edu.pl

Dedicated to Prof. Jacek Mlochowski on the occasion of his 80th anniversary

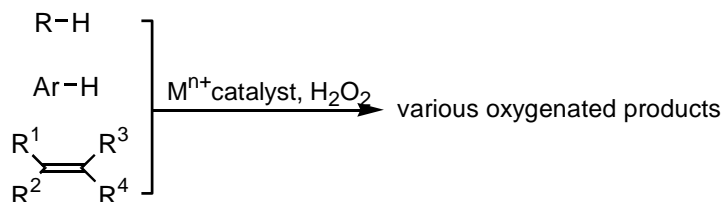
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Abstract

This review presents the current state of the art of homogenic and heterogenic oxygen transfer processes using hydrogen peroxide as oxygen source and compounds and complexes of transition metals, Fe, V, Cu, Mn, Rh, Mo, Ti, W, Pd, Os, Zr, Cr, Nb, Co, as the catalysts. Based on the reactions of C-H, C-C and C=C bonds in alkanes, arenes and alkenes various mechanisms of the oxygen-transfer processes are discussed and new methodologies for synthesis of alcohols, phenols, aldehydes, ketones, epoxides and carboxylic acids are indicated.



Keywords: Oxidation, hydrogen peroxide, organic synthesis, catalysis

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Introduction

Oxidation reactions are of fundamental importance in nature, and are key transformations in practical organic synthesis, in both laboratory and industry. The development of processes that employ hydrogen peroxide as an environmentally friendly oxidant is one of the most important goals in oxidation chemistry. Hydrogen peroxide is supplied mainly as a 30% aqueous solution. It is relatively stable, easy to store, commercially available and relatively cheap reagent of low molecular weight which can be used on any scale. It contains a large amount (40% by weight) of active oxygen (next after O₂), much more than other oxidants. The standard reduction potential $E^\circ=1.776\text{ V}$ is higher than that of dichromates in acidic medium. Hydrogen peroxide by itself is only moderately reactive towards most organic substrates, and in some reactions with electrophiles it reacts as a nucleophile rather than an oxidant.¹⁻⁶

The most common oxidation catalysts contain a transition metal that activates hydrogen peroxide for the oxyfunctionalization of the organic substrate. The broad spectrum of applications of metal catalysts for hydrogen peroxide oxidation have been reviewed elsewhere e.g. in refs 7-18. Alternatively, one may perceive the use of organocatalysts and enzymes, which mediate catalytic homogenous oxidations without the need for metal-containing catalysts. These include α -hydroxyperoxides, hydroperoxyflavines, imine-derived hydroperoxysulfonyl amides (e.g. α -hydroperoxycamphorsulfonyl amides) and oxaziridines, amino acids, cyclodextrins, selenium and tellurium compounds, and other compounds.^{17,19-24}

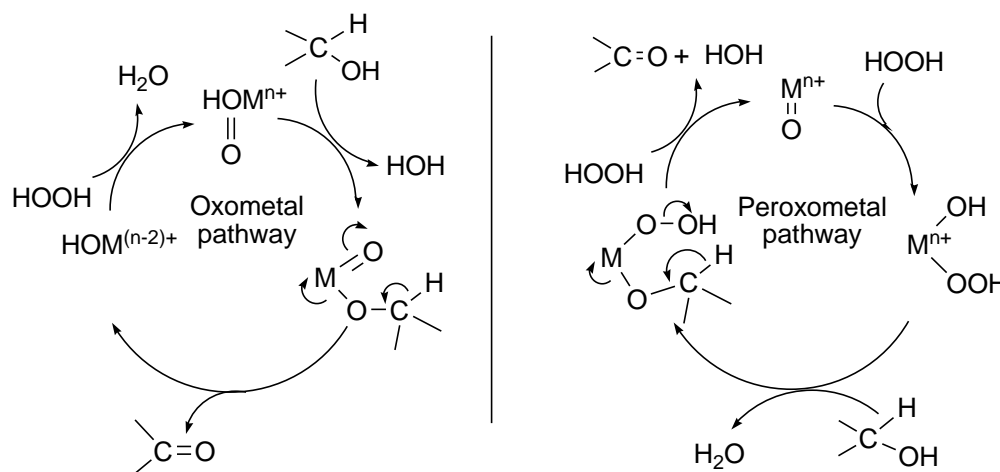
Following the discovery of a broad spectrum of new metal catalysts for hydrogen peroxide oxidation in recent years, and the huge progress in their use in organic synthesis, this review covers the scientific literature from 2011 to early 2016, but includes a few significant earlier references where necessary to the discussion. Since, during this period, hundreds of articles covering this topic have been published, this presentation is limited to those catalysts which meet the conditions defined by Gladysz,²⁵ make the greatest impact on modern practical synthesis, and allow an understanding of the reaction mechanisms.

Among oxyfunctionalizations of various groups of organic compounds, oxidation of hydrocarbon C-H, C-C and C=C bonds is a fundamental problem in the synthetic laboratory and industrial chemistry because this group of compounds is derived from natural sources on a large scale and their transformations lead to many products used in modern technologies and medicine. This review focuses on the use of metal-containing catalysts for oxidation of hydrocarbons, but some oxidations of hydrocarbon moieties in more complex compounds are also mentioned. Procedures for the preparation of the catalysts and analysis of their structures can be found in the cited literature

2. Metal Catalysis: Mechanistic Considerations

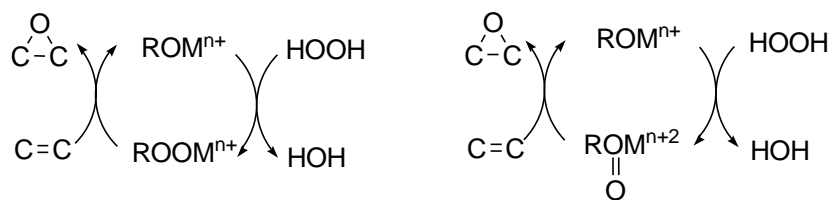
2.1 Oxometal vs. peroxometal pathways

Metal-catalyzed oxidations with hydrogen peroxide can be conveniently divided into two categories, involving peroxometal and oxometal species, respectively, as the active oxidant. An illustrative example is given for alcohol oxidations in Scheme 1. In the peroxometal pathway, the metal ion does not undergo any change in oxidation state during the catalytic cycle, and no stoichiometric oxidation is observed in the absence of H_2O_2 . In contrast, oxometal pathways involve a two electron change in oxidation state of the metal ion and a stoichiometric oxidation is observed, with the oxidized state of the catalyst, in the absence of H_2O_2 . Indeed, this is a test for distinguishing between the two pathways. Peroxometal pathways are typically observed with early transition metal ions with a d^0 configuration, e.g. Mo(VI), W(VI), Ti(IV), Re(VII), that are relatively weak oxidants. Oxometal pathways are characteristic of late transition elements and first row transition elements, e.g., Cr(VI), Mn(V), Os(VIII), Ru(VI) and Ru(VIII), that are strong oxidants in their highest oxidation states.^{1,26,27}



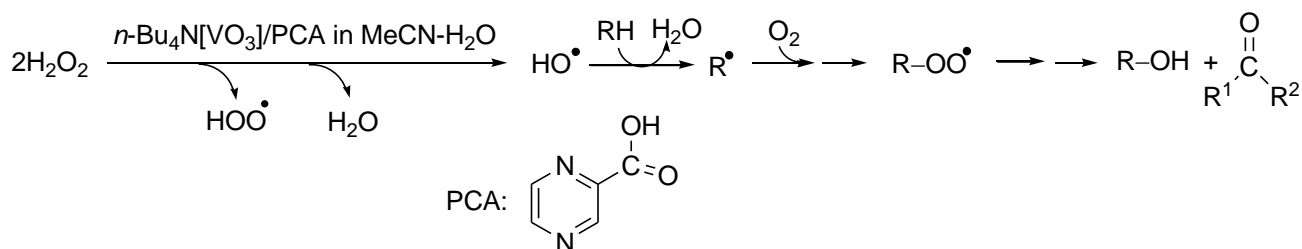
Scheme 1. Oxometal and peroxometal pathways in oxidation of alcohols.

Analogously, peroxometal and oxometal pathways have been postulated in the oxidation of hydrocarbons, e.g. in epoxidation of alkenes, with hydrogen peroxide and alkyl peroxides (Scheme 2).



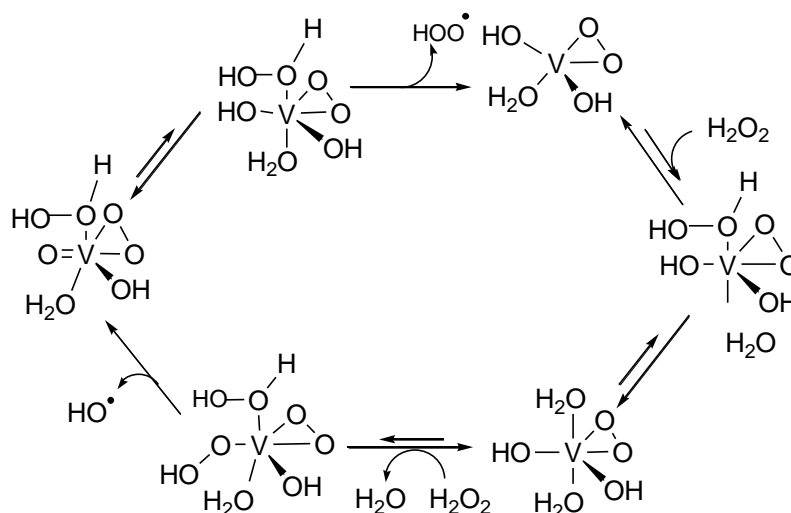
Scheme 2. Peroxometal and oxometal pathways in alkene epoxidation.

It is also worth noting that an oxometal intermediate can be formed via heterolysis of the O-O bond of an initially formed peroxometal species. The metal ion increases the oxidizing power (electrophilicity) of the peroxy moiety by withdrawing electrons, *i.e.* by acting as a Lewis acid. Hence, the peroxometal pathway is not limited to variable-valence elements. In the oxometal pathway, in contrast, the metal center undergoes a two electron reduction and is subsequently reoxidized by the oxygen donor. Some metals can operate *via* both pathways, depending on the substrate, e.g. vanadium(V) operates via a peroxometal pathway in olefin epoxidations and via an oxometal pathway in alcohol oxidations. It was shown that simple monovanadate VO_3^- efficiently catalyzes the oxidations of alkanes, benzene, and styrene with H_2O_2 in acetonitrile, if pyrazine-2-carboxylic acid (PCA) is added as a cocatalyst in a low concentration. Kinetic studies and DFT calculations have demonstrated that the mechanism of this process involves the formation of HO^\bullet and HOO^\bullet radicals. The former highly reactive radical abstracts the hydrogen from alkane RH , to give radical R^\bullet , which upon reaction with O_2 affords the corresponding alkyl hydroperoxide, ROO^\bullet . This not a very stable species and can easily be transformed into the industrially useful alcohol or ketone (Scheme 3).²⁸



Scheme 3. Overall radical mechanism of the catalyzed oxidation of alkanes by H_2O_2 .

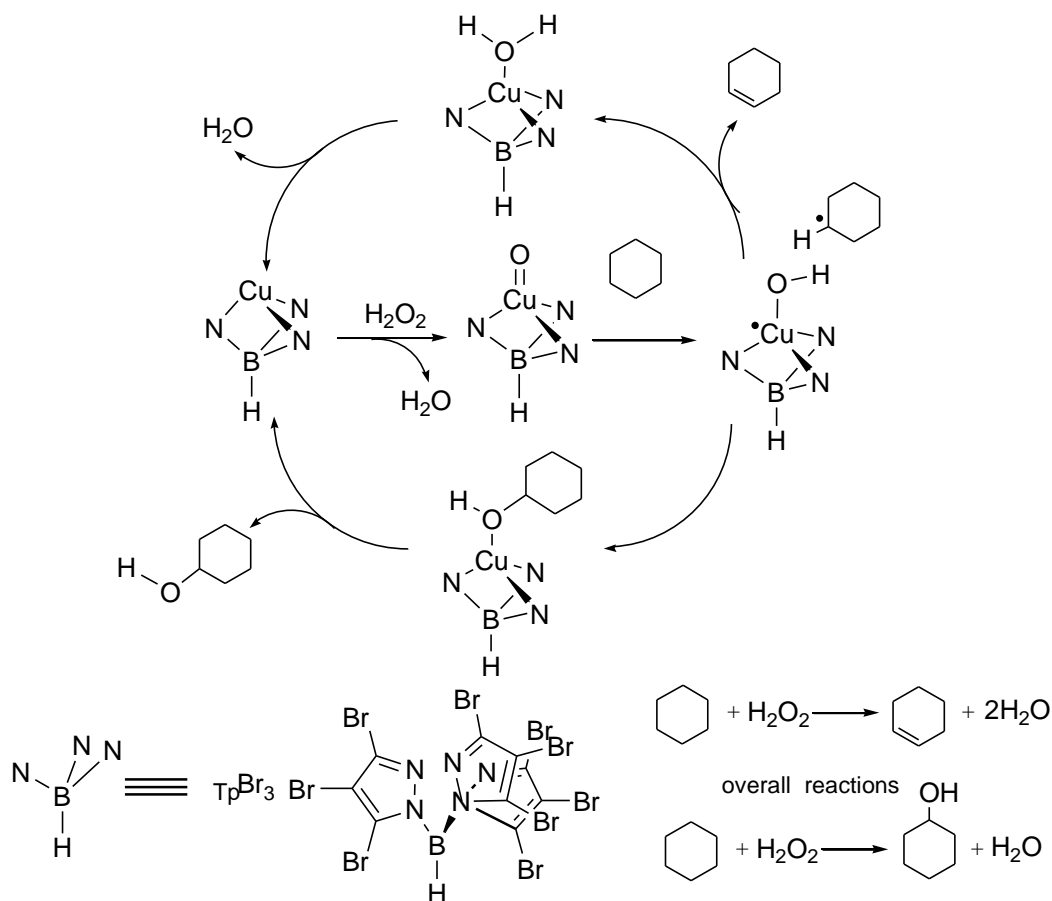
The vanadium-catalyzed oxidations of alkanes are very sensitive to the presence of H^+ in the reaction mixture. Simple monovanadate VO_3^- does not exhibit any catalytic activity toward alkanes, but the addition of an acid in low concentration dramatically accelerates this reaction. The hypothesis of the formation of oligovanadates in acidic medium, which are more active toward the oxidation of alkanes than the simple monovanadate, was confirmed by both experimental and theoretical methods. ^{51}V NMR and kinetic studies indicate, that in the systems $\text{VO}_3^-/\text{H}_2\text{O}_2/\text{TFA}$ and $[\text{V}_{10}\text{O}_{26}]^{4-}/\text{H}_2\text{O}_2$ in acetonitrile, oligovanadates are responsible for the efficient generation of hydroxyl radicals (key species in the alkane oxidation) (Scheme 4).^{29,30}



Scheme 4. Catalytic cycles for the formation of HOO^\bullet and HO^\bullet radicals based on μ -oxo vanadium complexes.

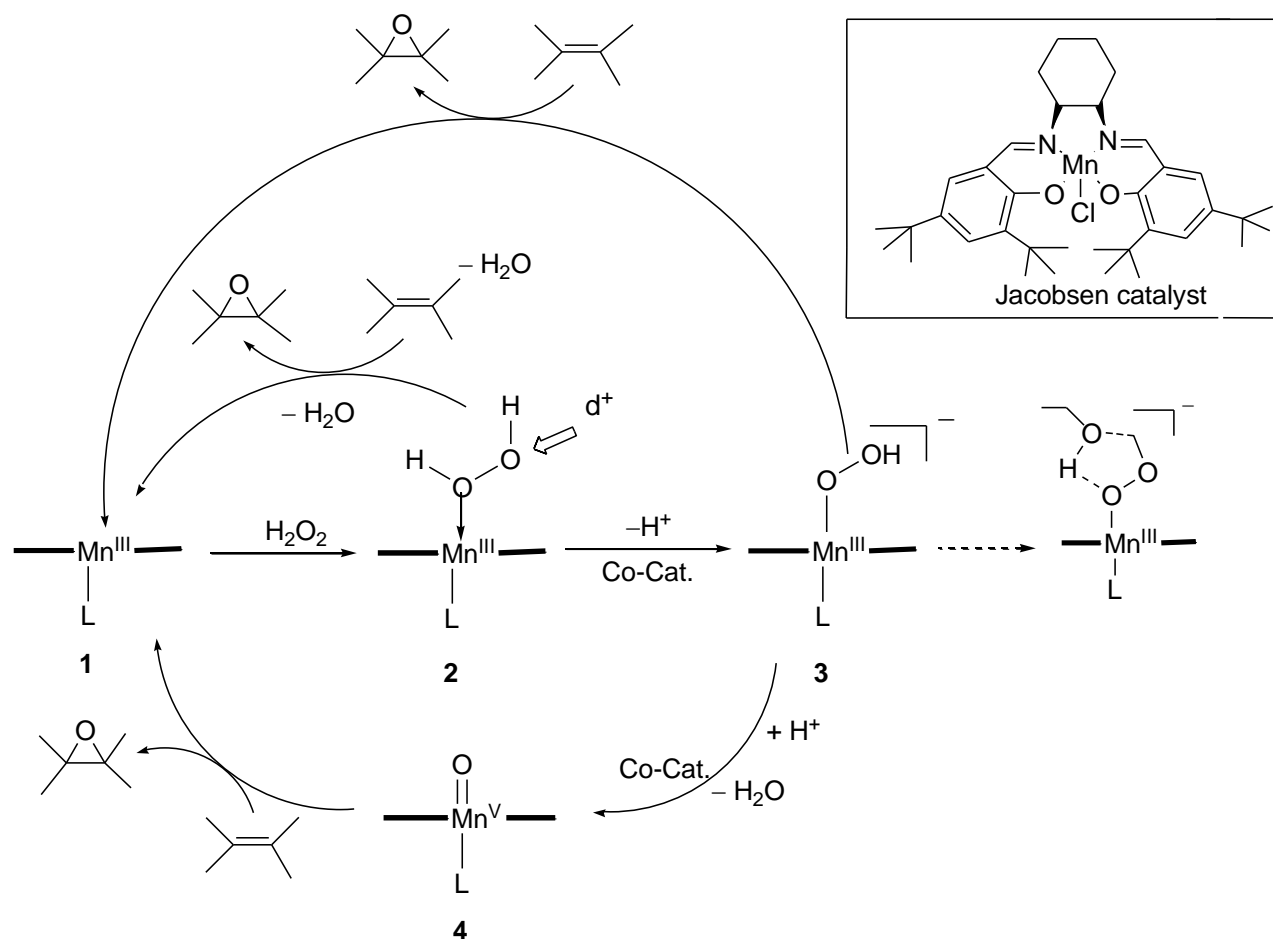
On the basis of the experimental and theoretical data on copper-catalyzed oxidative alkane dehydrogenation, the mechanistic proposal shown in Scheme 5 was formulated. The trispyrazolylborate (Tp^xCu) core reacts with hydrogen peroxide via an oxometal pathway, to give a copper-oxo intermediate with strong oxyl character. Interaction with cyclohexane induces a hydrogen abstraction process, yielding the cyclohexyl radical and $\text{Tp}^x\text{Cu}-\text{OH}$. From here, two competitive pathways may occur. Through the hydroxylation pathway, the cyclohexyl radical collapses with $\text{Tp}^x\text{Cu}-\text{OH}$ leading to cyclohexanol formation, whereas through the dehydrogenation pathway, a second hydrogen abstraction from the α C-H of the cyclohexyl radical, leads to cyclohexene formation. In the latter case, the oxidant itself acts as hydrogen acceptor, with the net reaction providing two molecules of water from one molecule of H_2O_2 and cyclohexane. These pathways involve spin crossover through MECPs of similar energy, which leads to product mixtures. The lowest-energy MECP yields cyclohexanol as major reaction product. None of these pathways involve the formation of free hydroxyl radicals.³⁰

Studies on catalytic oxidation of benzene to phenol over CuO -impregnated mesoporous silica provided the evidence that the reaction path involves a first stage, where the interaction of $\text{Cu}/\text{MCM-41}$ catalysts with H_2O_2 yields HO^\bullet radical and HOO^\bullet radical species via a redox mechanism. Next, the HO^\bullet radical attacks the benzene ring and yields phenol as the major product, with hydroquinone and benzoquinone as the side products. Oxygen and water are formed as side products by the decomposition of the hydroperoxy radical and H_2O_2 , respectively. So the process mainly follows a free radical mechanism.^{31,32}



Scheme 5. The mechanism of copper-catalyzed oxidative alkane dehydrogenation.

Mechanistic consideration of enantioselective vinylarene (indene, chromene, styrene) epoxidation, under mild conditions by the Mn(III)-containing Jacobsen catalyst, led to the conclusion that activation of H_2O_2 by this complex is similar to activation of H_2O_2 by other metal complexes, namely metalloporphyrins and by peroxidase. Upon addition of hydrogen peroxide to the catalyst **1**, the peroxy group is activated through formation of a [Mn(III)salen- H_2O_2] adduct **2** (Scheme 5), which by deprotonation leads to a hydroperoxy intermediate [Mn(III)salen-OOH] **3**. Next, the hydroperoxy intermediate **3** can undergo protonation and dehydration, generating the oxo-species **4**. The hydroperoxy species is able to epoxidize olefins through a concerted mechanism, as observed for the epoxidation by peracids, namely *m*-CPBA, since the electrophilicity of the distal peroxidic oxygen is enhanced due to metal bond activation. On the other hand, the activity of the oxo-species **4** was found to be high. Independent of the oxidant used it was considered to be the intermediate mainly responsible for the high enantioselectivity of the Jacobsen catalyst, relative to other systems. It is a consequence of the close proximity of the active oxygen to the non-planar and hindered salen ligand, schematically represented in Scheme 6.³³

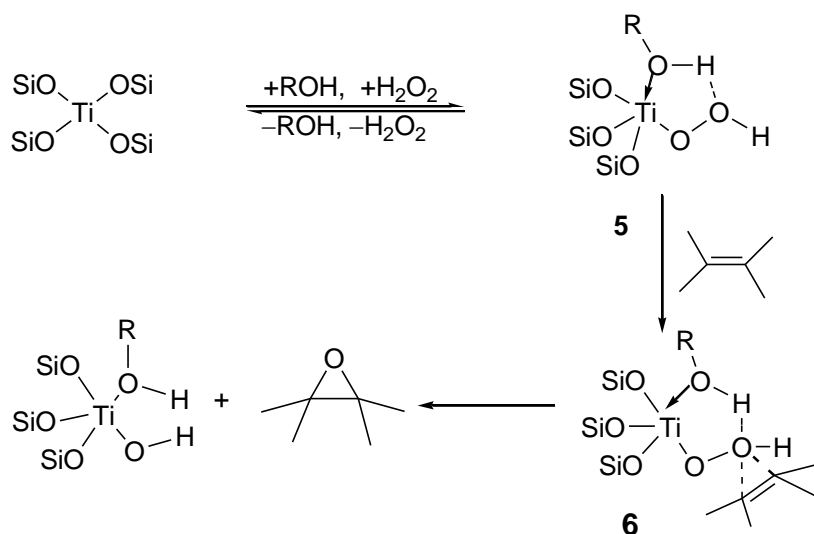


Scheme 6. Hydrogen peroxide enantioselective epoxidation of vinylarenes under mild conditions by the Jacobsen catalyst.

2.2 Solid supported catalysts

A broad range of solid supported catalysts including peroxometalates, framework-substituted microporous and mesoporous molecular sieves, layer-type materials, inorganic oxides, porous materials, encapsulated metal complexes, supported porphyrin and nanomaterials, have been reported during last decades as catalysts suitable for liquid phase oxidation with H₂O₂. Among these, catalyst systems with W, Ti and Mo have much better prospects of industrial applications. Due to their exclusive properties of oxidation of various types of organic compounds, much work has been devoted to the reaction mechanisms.³⁴⁻³⁸

Due to the exclusive properties of titanosilicates, especially TS-1, on oxidation of different groups of organic compounds, the mechanisms of their action have been extensively studied. They vary depending on the microstructure of the catalyst and the substrate used. In the TS-1 catalyst, titanium is tetrahedrally coordinated, which coordinates a protic solvent such as alcohol and is transformed into pentahedral and/or octahedral coordination. Increasing the size of the R group in the alcohol facilitates the formation of hydroperoxide intermediate **5** and favors the approach of the alkene. The oxygen atom is transferred to the alkene C=C bond by intermediate complex **6** and an epoxide is formed, as shown in Scheme 7.^{39,40}

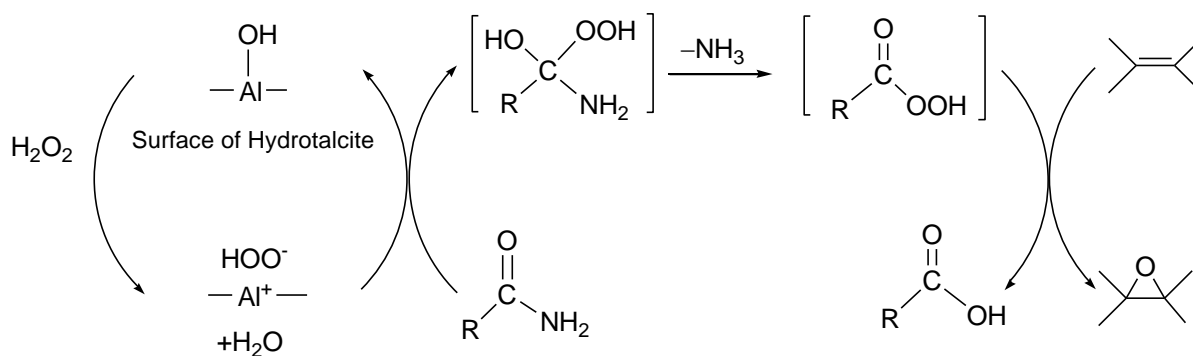


Scheme 7. Titanosilicate (TS-1) epoxidation of olefins.

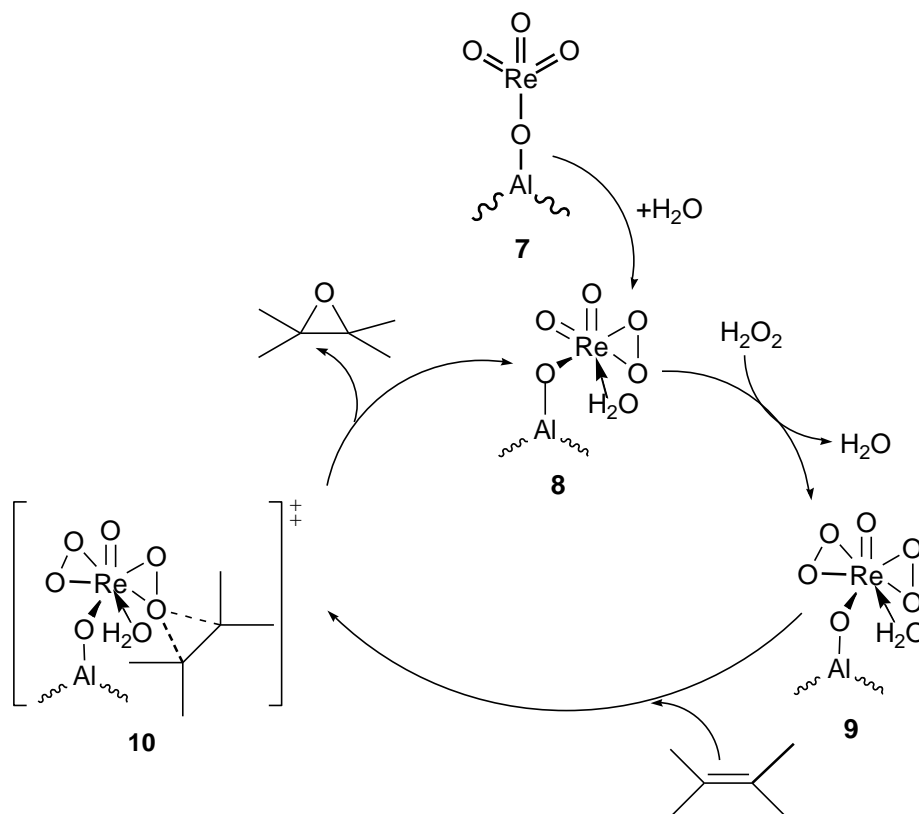
Normally, titanium–silicates produce products typical of both two-electron oxidation mechanisms (cyclohexene epoxide and *trans*-cyclohexane-1,2-diol), and one-electron oxidation mechanisms (cyclohex-2-en-1-ol and cyclohex-2-en-1-one). A Ti-hydroperoxide with a Ti-OOH bond is formed by the chemisorption of hydrogen peroxide on Ti-sites. This can be the active species in a heterolytic mechanism as in the oxidation of olefins and possibly of alcohols or the precursor of a Ti-centred radical species, responsible for homolytic oxidations, as in the hydroxylation of alkanes and in the decomposition of hydrogen peroxide. The adsorption of a protic component of the solution, affects the activity of active species. The direction of the oxidation path is determined by a combination of different factors: the nature of catalyst surface, the polarity of the solvent, the reactivity of the substrate and the temperature. On these grounds, a general oxidation mechanism was proposed for TS-1 and other Ti-zeolites.^{41,42}

The metal hydroperoxide was also postulated as an active intermediate formed during the epoxidation, catalyzed by layered hydrotalcite in the presence of isobutyramide (Scheme 8). Hydrogen peroxide attack a basis hydroxyl function of the aluminium atoms on the surface of hydrotalcite to form hydroperoxy species, which react with an amide, to generate a peracid together with NH₂ in the aqueous phase. Further, oxygen transfer from the peracid to an alkene occurs at the surface boundary between aqueous and organic phases, hence addition of an anionic surfactant is preferred. When the Mg/Al reaction was carried in the presence of acetonitrile the iminoperacetic acid, formed *in situ*, was an active oxygen donor.^{43,44}

The reaction mechanism of the Al₂O₃/H₂O₂-catalyzed alkene epoxidation probably involves an Al-OOH species, which react with alkene to give the resulting peroxide.^{45,46} In the rhenium-catalyzed epoxidation of alkenes on the surface of alumina, the tetrahedral ReO₄⁻ species are attached to alumina surfaces by covalent Al-O-Re bonds. Reaction on surface-Al-O-ReO₃ **7** gives the peroxy species **8**, which reacts further with H₂O₂ to form complex **9**. Oxygen transfer from **9** to the alkene C=C bond, yields the epoxide via intermediate complex **10** (Scheme 9).⁴⁷



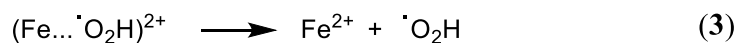
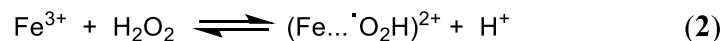
Scheme 8. Proposed mechanism for the hydrotalcite-catalysed epoxidation of olefins with isobutyramide (R = Me₂CH.CH₂) as additive.



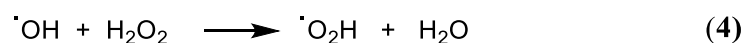
Scheme 9. Proposed mechanism for the Re-catalyzed epoxidation of alkenes on the surface of alumina.

2.3 The Fenton reaction

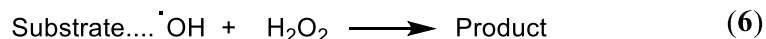
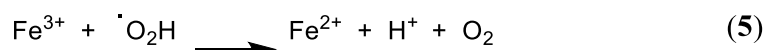
The well-known Fenton reaction is the reaction between ferrous ion and hydrogen peroxide, resulting in the formation of hydroxyl and perhydroxyl radicals and ferric ion Equations (1-3). The ferric ion with the hydrogen peroxide generate a complex, which is the ferrous ion coordinated with perhydroxy radical, which decomposes to ferrous ion and perhydroxy radical as seen in Equations (2) and (3). This regenerative nature is characteristic of the Fenton reagent.



On the other hand, the perhydroxyl radicals can be formed from hydrogen peroxide and hydroxyl radical, directly generated in the reaction between the ferrous ion and H_2O_2 Equation (4).



The hydroxyl radicals are more selective than perhydroxyl radicals with organic compounds and it was assumed that it is the hydroxyl radicals that take part in the oxidation of organic compounds Eq. (6), while the perhydroxyl radicals decompose to molecular oxygen Eq. (5) and it was assumed that an addition complex is formed between the substrate (e.g. phenol) and the hydroxyl radical.⁴⁸



3. Oxidation of C-H, C-C and C=C Bonds

3.1 Oxidation of alkanes

The selective oxidation of alkanes and arenes remains a fundamental problem in organic synthesis, because their components, carbon and hydrogen, do not have lone electron pairs and the molecules do not have orbitals of sufficient energy, that are easily accessible. When very reactive reagents are used and the reaction is carried out under harsh conditions, the initial products are generally more reactive than the starting compounds and undesired side reactions occur. Despite extensive development, efforts to find new catalysts for alkane and arene oxidation, current commercial processes still suffer from low conversion, poor selectivity and excessive production of waste. Thus, high-efficiency and high-selectivity catalytic oxidation of C-H groups under mild conditions is a major objective of current catalysis and remains one of the greatest challenges in organic synthesis.

In recent years, significant progress has been made in the oxidation of hydrocarbons with hydrogen peroxide in the presence of vanadium, copper, iron, osmium, tungsten, manganese, molybdenum, cobalt compounds and complexes. Vanadium compounds have attracted much attention, because they have been used widely for homogeneous, heterogeneous, industrial, and biological oxidation processes with H_2O_2 , alkyl hydroperoxides, and O_2 . Reactions of vanadium complexes and vanadium-containing polyoxometalates (POMs) with H_2O_2 have been extensively studied and several mono-, di-, and poly-nuclear peroxovanadium complexes have been isolated and characterized. The isolated and/or in situ-generated peroxovanadium complexes catalyze H_2O_2 -based oxidation of alkanes, as well as alcohols, aromatic compounds, sulfides, and halides. The new hexanuclear mixed-valence vanadium complex $[\text{V}_3\text{O}_3(\text{OEt})(\text{ashz})_2(\mu\text{-OEt})]_2$ ($\text{ashzH}_3 = N\text{-acetyl-}$

salicylhydrazide), with an N,O-donor ligand, acts as a highly efficient catalyst toward alkane oxidations by aqueous H₂O₂. Remarkably, high turnover numbers up to 25,000 with product yields of up to 27% (based on alkane), being one of the most active systems for such reactions.⁴⁹ The efficient oxidation of alkanes (cyclohexane, *n*-heptane, methylcyclohexane, isooctane, *cis*- and *trans*-1,2-dimethylcyclohexane) to the corresponding alkyl hydroperoxides with the system (*n*-Bu₄N)[VO₃]/H₂O₂/trifluoroacetic acid/MeCN-H₂O was investigated and it has been established on the basis of the cyclohexane oxidations, that the reaction mechanism includes the formation of HO· radicals.⁵⁰

The oxovanadium(IV) complexes [VO(acac)₂(Hpz)]·HC(pz)₃ I (acac = acetylacetonate, Hpz = pyrazole, pz = pyrazolyl) and [VOCl₂{HOCH₂C(pz)₃}] II under either heterogeneous (immobilized on a PDMS-based membrane) or homogeneous conditions, exhibit appreciable catalytic activity for the oxidation of cyclohexane to cyclohexanol/cyclohexanone mixtures. The stoichiometric oxidant was H₂O₂, or better more active benzoylperoxide or *m*-chloroperbenzoic acid in acetonitrile in acidic medium, at room temperature, in moles products/moles catalyst ratios (TONs) up to 1100.⁵¹ The same authors reported the catalytic activity of transition-metal complexes of the first-row (V(IV), Mn(III), Fe(III) Co(III) and Cu(II)) with biomimetic Schiff base ligands with N₂O₂ coordination sphere in the room-temperature oxidation of cyclohexane using hydrogen peroxide 30% H₂O₂ as the oxygen source, acetonitrile as the solvent and nitric acid as promoter of the oxidation reaction.⁵² A new binuclear oxovanadium(V) complex [{VO(OEt)(EtOH)}₂L], where H₄L was bis(2-hydroxybenzylidene)terephthalohydrazide, was synthesized and used in combination with pyrazine-2-carboxylic acid (PCA; a cocatalyst) for the efficient oxidation of saturated hydrocarbons RH, with H₂O₂ and air in acetonitrile solution at 50 °C, to produce alkyl hydroperoxides ROOH, as the main primary products.⁵³ The catalytic performances of three new peroxy- and oxovanadium(IV) complexes: [VO(O₂)(bpz*eaT)·VO(C₄H₄O₆)]·H₂O, [VO₅O₄(bpz*eaT)]·C₆H₈O₇ (bpz*eaT=2,4-bis-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-diethylamino-1,3,5-triazine) and [VO(C₁₂H₈N₂)(C₉H₇NO₃)]·MeOH·0.5H₂O, were studied in the reaction of cyclohexane oxidation. The first of them exhibited the highest catalytic activity.⁵⁴

Two novel oxomolybdenum(V)-trispyrazolylborate complexes [(TpMoO)(μ₂-O)₂(MoOTp)](Tp = tris(pyrazolyl)borate) and [(Tp4IMoOCl)(μ-O)(MoOCITp4I)](Tp4I = tris(4-iodinpyrazolyl)borate) were synthesized and characterized. Their catalytic performances in cyclohexane oxidation were significantly better than the molybdenum(VI) complexes with the similar structure.⁵⁵

A promising approach for mild oxidative functionalization of alkanes, concerns the development of bio-inspired metal complex catalysts which, with an appropriate oxidizing agent and under tuned reaction conditions, are capable of converting alkanes into valuable functionalized products. In view of the well recognized biological function of copper, which is present in the active sites of many oxidation enzymes, several complexes were prepared and used as catalyst while the oxide source was hydrogen peroxide.⁵⁶ The dehydrogenation of *n*-hexane and cycloalkanes, giving *n*-hexene and cycloalkenes, was observed in the reaction of such hydrocarbons with hydrogen peroxide in the presence of copper complexes bearing trispyrazolylborate ligands. Experimental data exclude the participation of hydroxyl radicals derived from Fenton-like reaction mechanisms.³⁰

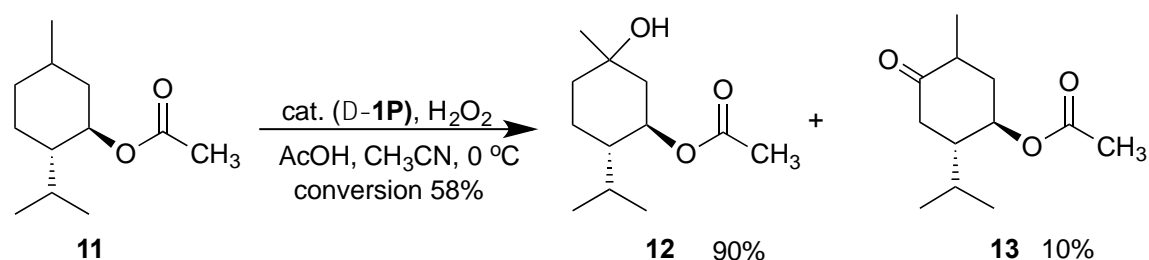
The photocatalytic conversion of methane into methanol from an aqueous suspension containing mesoporous WO₃ was studied, as well as the effect of the addition of electron scavengers (Fe³⁺, Cu²⁺, Ag⁺) and H₂O₂ species. In the presence of Fe³⁺ ions the production of methanol was about two and a half times higher than that of pure mesoporous WO₃.⁵⁷

The tricopper complex [CuI₃CuI(7-N-Etppz)]¹⁺, where 7-N-Etppz denotes the ligand 3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-Et-piperazine-1-yl)propan-2-ol], is capable of mediating facile conversion of methane into

methanol, upon activation of the tricopper cluster by dioxygen and/or H₂O₂ at room temperature. This is the first catalyst that can catalyze selective oxidation of methane to methanol, without over-oxidation, under ambient conditions. When this tricopper complex is activated by dioxygen or H₂O₂, the tricopper cluster harnesses a "singlet oxene", the strongest oxidant that could be used to accomplish facile O-atom insertion across a C-H bond. To elucidate the properties of this novel catalytic system, methane oxidation over a wide range of conditions was investigated and the study was extended to other small alkanes, including components of natural gas.⁵⁸ Continuous selective oxidation of methane to methanol and production of C₂ oxygenated products from ethane using H₂O₂ as an oxidant over Cu- and Fe-modified ZSM-5 catalysts, was reported. A trickle bed continuous flow reactor was utilized to control the contact time effectively between reactants and catalyst, to minimise C-C scission and over oxidation to CO_x.^{59,60} Titania-supported gold palladium copper AuPdCu/TiO₂ catalysts are able to catalyze the oxidation of methane to methanol with H₂O₂ under mild aqueous reaction conditions, with methanol selectivity of up to 83%.⁶¹

The Cu(I) compound [Cu(μ₄-4-ptz)]_n [1,4-ptz = 5-(4-pyridyl)tetrazolate] revealed high catalytic activity toward oxidation of cyclic alkanes (cyclopentane, cyclohexane and cyclooctane) with aqueous hydrogen peroxide, under very mild conditions at room temperature.⁶² The catalytic peroxidative oxidation (with H₂O₂) of cyclohexane in an ionic liquid (IL) using the tetracopper(II) complex [(CuL)₂(μ₄-O,O,O,O-CDC)]₂·2H₂O [HL = 2-(2-pyridylmethyleneamino)benzenesulfonic acid, CDC = cyclohexane-1,4-dicarboxylate] as a catalyst was reported. Significant improvements on the catalytic performance, in terms of product yield (up to 36%), TON (up to 529), reaction time, selectivity towards cyclohexanone and easy recycling were observed using 1-butyl-3-methylimidazolium hexafluorophosphate as the chosen IL instead of a molecular organic solvent including the commonly used acetonitrile.⁶³ The easily prepared Cu(II), Co(II) and Ni(II) complexes, immobilized on imine-functionalized silica gel through a 3-aminopropyltriethoxysilane linker, were reported as efficient catalysts for cyclohexane oxidation to cyclohexanol and cyclohexanone under ambient conditions.⁶⁴ The mononuclear water-soluble copper(II) complexes of pyridine 2-carboxamide, were reported as suitable catalysts for the oxidation of toluene, ethylbenzene and cyclohexane.⁶⁵ The novel water-soluble 2D copper(II) coordination polymers were found to be highly active precatalysts for the mild water-promoted oxidation of cycloalkanes, from cyclopentane to cyclooctane, with 50% aqueous hydrogen peroxide to mixtures of alcohols and ketones in 16.5-35.8% yields.⁶⁶

A family of imine-based nonheme iron(II) complexes (LX)₂Fe(OTf)₂ has been prepared, characterized and employed as C-H oxidation catalysts. Ligands LX (X = 1, 2, 3, and 4) stand for tridentate imine groups, resulting from spontaneous condensation of 2-picolylamine and 4-substituted-2-picolyl aldehydes. Reactions occur with stereoretention at the hydroxylated carbon and selectively at tertiary over secondary C-H bonds.⁶⁷ Mononuclear non-heme iron coordination complexes Λ-[Fe(CF₃SO₃)₂(S,S,R)-MCP)]], Δ-[Fe(CF₃SO₃)₂(R,R,R)-MCP)] (Δ-1P), Λ-[Fe(CF₃SO₃)₂(S,S,R)-BPBP)] and Δ-[Fe(CF₃SO₃)₂(R,R,R)-BPBP)] catalyze the fast, efficient, and selective oxidation of nonactivated alkyl C-H groups. Several branched alkanes and cycloalkanes were oxidized and regioselectivities determined with these catalysts. The oxidation of menthyl acetate **11** to alcohol **12** and ketone **13** is an example (Scheme 10).⁶⁸

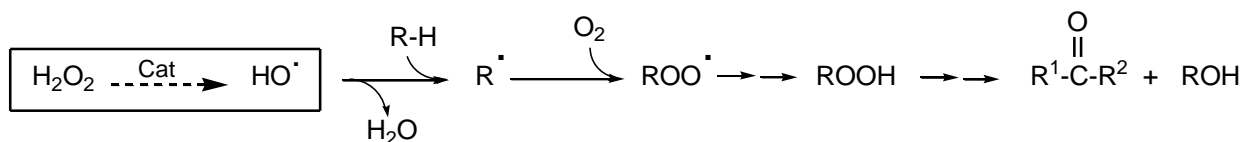


Scheme 10. Oxidation of menthyl acetate catalyzed by iron complex **Δ-1P**.

The efficient oxidation of alkanes to the corresponding alkyl hydroperoxides by H₂O₂ in the presence of catalytic amounts of ferrocene, proceeded in MeCN at 40-50 °C. Benzene was oxidized in the same system to phenol. An obligatory component of the catalytic system for both reactions is pyrazine-2-carboxylic acid (PCA) or trifluoroacetic acid (TFA).⁶⁹ Both alkanes (cyclohexane, adamantane, alkylarenes) and alcohols (isopropanol, cyclohexanol, benzyl alcohols), were selectively oxidized to their corresponding aldehydes and ketones in excellent yields with 30% H₂O₂, in the presence of eco-friendly, cheap and reusable polymer-anchored iron(III)-ferrocene Schiff base complex.⁷⁰ Supporting the iron-salen complexes on montmorillonite, affords active, selective and recyclable catalysts for the liquid phase oxidation of *n*-octane with hydrogen peroxide under mild conditions, with ketones as the major products, although conversions of the substrate were low (3.6-7.4%).⁷¹ The hydrotris(pyrazol-1-yl)methane iron(II) complex immobilized on commercial zeolite (MOR) or desilicated (MOR-D), catalyzes the oxidation of cyclohexane with hydrogen peroxide to cyclohexanol and cyclohexanone, under mild conditions. MOR-D/Fe (desilicated zeolite supported [FeCl₂{η³-HC(pz)₃}] complex) provides an outstanding catalytic activity (TON up to 2.90 × 10³) with a concomitant overall yield of 38%, and can be easily recovered and reused.⁷² When hexadentate binding 8-quinolinolato iron(III) complexes were used for the oxygenation of cyclohexane to cyclohexanol and cyclohexanone by aqueous H₂O₂ in acetonitrile, the reactions were accelerated to some extent by heating or under visible light irradiation. Based on UV-visible spectroscopic characterization, a free radical mechanism for this catalytic oxygenation system was proposed.⁷³

It was disclosed that two heteroleptic 8-quinolinolato iron(III) complexes (Qa₁Qb₂Fe^{III} and Qa₂Qb₁Fe^{III}) (synthesized conveniently via coordination of FeCl₂·6H₂O with suitable equivalents of 5,7-dichloro-8-hydroxyquinoline (Qb) or 5-chloro-8-hydroxyquinoline (Qa), showed catalytic activity in the oxygenation of cyclohexane to a mixture of cyclohexanol (0.3-10.% yield) and cyclohexanone (0.2- 12.8-yield) as well as in the hydroxylation of benzene to phenol, oxygination of toluene to benzaldehyde and ethylbenzene to acetophenone in yields up to 17.2%.⁷⁴

It was demonstrated that simple soluble Bi(III) salts – systems unexplored earlier in the homogeneous oxidation of alkanes – exhibit a pronounced catalytic activity in the homogeneous oxidation of these hydrocarbons with hydrogen peroxide. The yield of the oxygenates in the oxidation of cyclooctane, catalyzed by the aqueous system Bi(NO₃)₃/H₂O₂/HNO₃/CH₃CN, attains 32% and the TON reaches 112. The reaction has a free-radical character and proceeds via hydroperoxides, finally hydrolyzed to ketones the main final products. (Scheme 11).⁷⁵



Scheme 11. Radical mechanism of the Bi(III)salts-catalyzed alkane oxidation with H₂O₂ (the rate limiting step of the whole process is boxed).

An efficient and selective oxidation of secondary carbon-hydrogen sites (C-H methylene group) of alkanes, was described and the synthesis of the target compounds was achieved by using a low catalyst loading of an inexpensive, readily available iron catalyst [Fe(II)(CF₃SO₃)₂(mcp) mcp = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)cyclohexane-*trans*-1,2-diamine] and H₂O₂ as oxidant by a simple reaction protocol. Natural products were selectively oxidized and isolated in synthetically amenable yield. It is a particularly convenient tool to carry out alkane C-H oxidation on a preparative scale in a short reaction time. Reactants included 2,2-dimethylpropanoic acid *cis*-4-methylcyclohexyl ester, 3,7-dimethyl-1-octanol 1-acetate, (1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexanol acetate [(-)-menthyl acetate], (+)-neomenthyl acetate, linear heptane, (3*aR*,5*aS*,9*aS*,9*bR*)-dodecahydro-3*a*,6,6,9*a*tetramethyl[naphtho[2,1-*b*]furan] [(-)-ambroxide], (+)-sclareolide (sesquiterpene lactone), *cis*-decalin, (3β,5α)-3-cetyloxyandrostane-17-one (steroid, androstane).⁷⁶ Catalytic activity of the new iron(II) α-aminopyridine complexes was demonstrated in the oxidation of cyclohexane, activated methylene groups and secondary alcohols to the corresponding ketones using H₂O₂ and *t*-BuOOH as the oxidants.⁷⁷

Low temperature selective transformation of light alkanes of natural gas into useful products continues to be an important challenge in chemistry and industry. For this purpose, nitrido diiron phthalocyanines were recently identified as powerful oxidation catalysts, capable of oxidizing methane, benzene and transforming poly- and perfluorinated aromatic compounds with hydrogen peroxide. Acetic acid was obtained from ethane with selectivity up to 71%. Turnover number up to 58 and 50-65 % product yields can be achieved. The reactivities of C-H bonds in methane, ethane and propane were very similar, when the reaction was performed in water. In contrast, in dilute acidic solution the nitrido diiron phthalocyanine–H₂O₂ system, exhibits 5 times higher activity in the oxidation of a methane C-H bond compared to an ethane C-H bond.⁷⁸ A new μ-oxo diiron(III) complex of the lithium salt of the pyridine-based unsymmetrical ligand 3-[[3-[[bis(pyridin-2-ylmethyl)amino]methyl]-2-hydroxy-5-methylbenzyl](pyridin-2-ylmethyl)amino]propanoate (LiDPCMPMP), [Fe₂(μ-O)(LiDPCMPMP)₂](ClO₄)₂, was synthesized and the ability of the complex to catalyze oxidation of several alkanes and alkenes has been investigated by using CH₃COOH/H₂O₂ (1:1) as an oxidative system. Moderate activity in cyclohexane oxidation to cyclohexanol (18% yield) and cyclohexanone (15% yield), and in cyclohexene oxidation to epoxycyclohexane (13% yield), 2-cyclohexenol (15% yield) and 2-hydroxycyclohexanone (8% yield) was detected. The formation of a transient peroxy species, [Fe₂(O)(O₂)(LiDPCMPMP)₂]²⁺, which might be an intermediate in the metal-based component of the oxidation process, was suggested.⁷⁹

Catalytic and mechanistic insights of the low-temperature selective oxidation of methane over Cu-promoted Fe-ZSM-5 demonstrated, that this system is able to catalytically convert methane to methanol with turnover frequencies (TOFs) of over 14 000 h⁻¹ by using H₂O₂ as terminal oxidant.⁸⁰ The same authors reported that the oxidation with hydrogen peroxide of methane to methanol is effectively catalyzed by supported Au-Pd catalysts. The primary product is Me hydroperoxide formed from the reaction of H₂O₂ with radical ·CH₃.⁸¹ The Au nanoparticles/CQDs (CQD = carbon quantum dots) composite photocatalyst yields 64% conversion

efficiency and 99.9% selectivity for the green oxidation of cyclohexane to cyclohexanone, using H₂O₂ under visible light at room temp.⁸²

Benzylic, aliphatic C-H as well as tertiary C-H oxidation with hydrogen peroxide was efficiently catalyzed by a benzimidazole-based nonheme manganese complex in the presence of acetic acid as additive. For example, oxidation of ethylbenzene gave benzophenone in 70% yield.⁸³ Catalytic properties of a series of manganese(III) complexes, with tetradentate phenol- and pyridine-based ligands, on the oxidation of the C-H bond of diphenylmethane in the presence of hydrogen peroxide as a terminal oxidant at ambient conditions, were investigated. In this process, diphenylmethane was oxidized to the corresponding ketone and alcohol.⁸⁴ An *in situ* prepared manganese catalyst, based on manganese(II) salts, pyridine-2-carboxylic acid, and butanedione, was employed for hydrogen peroxide oxidation of C-H bonds at ambient temperatures. It provides good-to-excellent conversions of benzyl and alkyl groups as well as secondary alcohols with high turnover numbers (up to 10 000).⁸⁵

The triosmium dodecacarbonyl cluster Os₃(CO)₁₂ catalyzes oxidation of linear (*n*-heptane) and cyclic alkanes (cyclohexane, cyclooctane, methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexanes) to the corresponding cycloalkyl hydroperoxides by hydrogen peroxide in acetonitrile. Addition of pyridine leads to an acceleration of the process. Turnover numbers in the case of cyclooctane attain 6·10⁴ and turnover frequencies are up to 24,000 h⁻¹. The alkyl hydroperoxide partly decomposes in the course of the reaction to afford cyclooctanone and cyclooctanol.⁸⁶

Other efficient catalysts for the oxidation of alkanes (cyclohexane, *n*-heptane, methylcyclohexane, isooctane, *cis*- and *trans*-1,2-dimethylcyclohexane) to corresponding hydroperoxides, are osmium complexes containing *p*-cymene ligands. The yield of cyclohexyl hydroperoxide, based on cyclohexane, is up to 30%, which is also amongst the highest reported. The oxidation of cyclohexane at 60 °C after 24 h, gave a turnover number of 2·10⁵ and turnover frequencies of 10³ h⁻¹. These parameters are the highest ones, observed for catalytic oxidation of alkanes, and are even comparable to enzymatic oxidation. Although osmium compounds are rather expensive, they can be successfully employed in oxidation of hydrocarbons and alcohols by peroxides, because the reactions require only very low concentrations of the catalysts.^{87,88}

The osmium(VI) nitrido complex, [Os^{VI}(N)(L)(CH₃OH)]⁺ (L = *N,N'*-bis(salicylidene)-*o*-cyclohexyldiamine dianion) is an efficient catalyst for the oxidation of alkanes under ambient conditions using H₂O₂ as the oxidant. Alkanes are oxidized to the corresponding alcohols and ketones, with yields up to 75% and turnover numbers up to 2230. Experimental and computational studies are consistent with a mechanism that involves O-atom transfer from H₂O₂ to [Os^{VI}(N)(L)]⁺ to generate an [Os^{VIII}(N)(O)(L)]⁺ active intermediate.⁸⁹

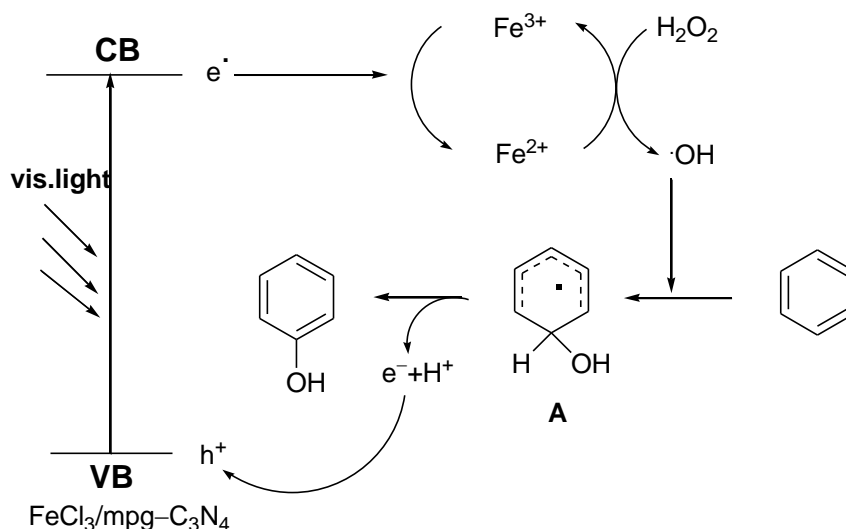
Isomeric cage-like tetracopper(II) silsesquioxane complexes [(PhSiO_{1.5})₁₂(CuO)₄(NaO_{0.5})₄] (a), [(PhSiO_{1.5})₆(CuO)₄(NaO_{0.5})₄(PhSiO_{1.5})₆] (b) and binuclear complex [(PhSiO_{1.5})₁₀(CuO)₂(NaO_{0.5})₂] (c), can be considered as models of some multinuclear copper-containing enzymes. Compounds (a) and (c) are good pre-catalysts for alkane oxygenation with hydrogen peroxide, in air in acetonitrile solution. Thus, the (a)-catalyzed reaction with cyclohexane at 60 °C, gave mainly cyclohexyl hydroperoxide in 17% yield.⁹⁰ The hybrid [DPyAM(H₂)]_{1.25}PMoV₂ was tested as a heterogeneous catalyst for the oxidation of cyclohexane by aqueous H₂O₂ (30 wt%) into a mixture of cyclohexanol as a major product and cyclohexanone as a minor one (total yield up to 31.9%), with acetonitrile as the solvent. The oxygenation of cyclohexane gives rise to the formation of alkyl hydroperoxide as the intermediate product, that is further decomposed to yield stable products, cyclohexanol and cyclohexanone.⁹¹

ZnO-supported Ag nanoparticles efficiently catalyzed the oxidation reactions of benzylic C-H bonds in alkyl-substituted arenes with H₂O₂.⁹² Selective oxidation of ethylbenzene using *tert*-butyl hydroperoxide and

H_2O_2 in the presence of mixed oxide spinels, derived from layered double hydroxides, gave acetophenone. The activity of the catalyst increased in the order $\text{MgCuMnAl} > \text{MgCoMnAl} \gg \text{MgMnAl} > \text{MgCrAl} > \text{CoMnAl}$ oxides.⁹³ The catalytic activity of SBA-15 supported Co_3O_4 , was evaluated in liquid phase benzylic oxidation with hydrogen peroxide under mild conditions. The benzylic oxidation was ascribed to hydrogen abstraction of the C-H bond. The 5 wt% of catalyst was found to exhibit high conversion (75%), with product selectivity of 87%.⁹⁴ The SiO_2 -included cesium polyoxotungstate and titanasilicate were also reported as efficient catalysts for oxidation of cyclohexane to cyclohexanol and cyclohexanone under mild conditions in liquid phase.⁹⁵ Titanium silicalite with hollow structure (HTS), is a new type of titanasilicate used in oxidation process. Its catalytic property on the mild oxidation of cyclohexane with hydrogen peroxide (H_2O_2) in liquid phase was investigated, and the difference of catalytic performance between HTS and compared sample (TS-1) discussed. Cyclohexanone and cyclohexanol were the major products.⁹⁶

3.2. Oxidation of arenes

Most recently published works on the synthetic application of arenes with hydrogen peroxide concern the reactions catalyzed by iron, copper and vanadium compounds. The FeCl_3 and mesoporous carbon nitride hybrid ($\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$) was reported as an active and selective photocatalyst to activate H_2O_2 for the oxidation of benzene to phenol under visible-light illumination. By fine-optimizing of the FeCl_3 loading amount in catalyst and reaction conditions, the one-step process achieved a 38% benzene conversion with high 97% selectivity for phenol. The excellent catalytic performance of $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ should be attributed to the fast reduction of Fe^{3+} to Fe^{2+} by photo-irradiated electrons from mpg- C_3N_4 . A plausible reaction path for the oxidation of benzene by the $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ system is illustrated in Scheme 12. The visible-light-induced catalytic cycle is assumed to involve two coupled steps: (1) the light-irradiated electrons from the CB of $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ reduce Fe^{3+} to Fe^{2+} , which could smoothly decompose H_2O_2 with the formation of active $\cdot\text{OH}$ radical; (2) the hydroxylation of benzene by $\cdot\text{OH}$ radical, produces a cyclohexadienyl radical intermediate **A** and then the positive hole of mpg- C_3N_4 (h^+) with moderate oxidation potential oxidizes **A** to yield phenol as the product. This environmental-friendly and efficient method could be a new avenue for one-step phenol preparation.⁹⁷



Scheme 12. A possible reaction mechanism for the catalytic oxidation of benzene by $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ hybrids.

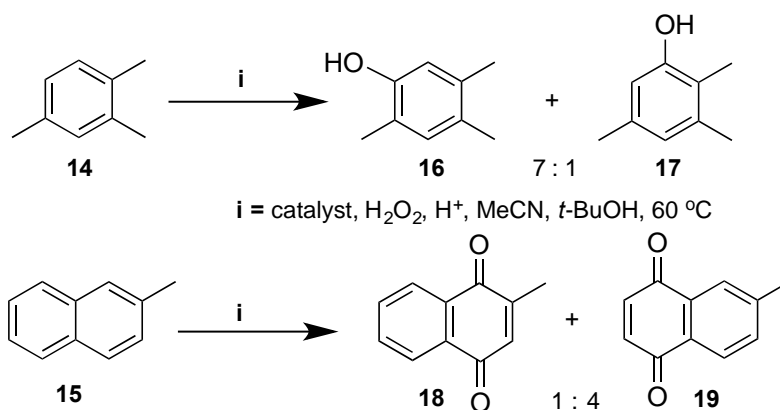
Other iron-containing hybrid materials, such as $\text{Fe-mpg-C}_3\text{N}_4$ (denoted as Fe-CN) and titanium silicate zeolite (TS-1), could be used as heterogeneous catalysts for the photocatalytic selective oxidation of benzene

to phenol using H_2O_2 , as benign oxidant under ambient conditions. It was found, that Fe-CN/TS-1 shows superior photocatalytic performance for phenol production from benzene to Fe-CN and TS-1 catalysts alone. Under the optimal conditions, up to 10% phenol yield (based on benzene) is achieved over the hybrid materials, with 18.4% phenol selectivity (based on H_2O_2).⁹⁸ Highly selective benzene hydroxylation to phenol can be achieved over two Fe-based metal-organic frameworks [MIL-100(Fe) and MIL-68(Fe)] under visible light irradiations using H_2O_2 as an oxidant. An optimal benzene conversion of 30.6% was achieved with a H_2O_2 :benzene ratio of 3:4 over MIL-100(Fe) after irradiation for 24 h.⁹⁹ In another heterogenous photo-Fenton system, with ferrocene-modified carbon nitride as the synergistic donor-acceptor, interaction between the carbon nitride matrix and ferrocene group, also improved exciton splitting, and coupled photocatalytic performance allowed the direct synthesis of phenol from benzene in the presence of H_2O_2 under visible light irradiation.¹⁰⁰

The promotional effect of nanosized Fe (also Ru, Au, and Mn) particles on $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (VHP) catalytic properties, was investigated in benzene hydroxylation with H_2O_2 . Catalytic results indicated a profound effect of the nanoparticle dopants on VHP catalyst activity and product distribution. Among the promoted VHP catalysts, Au/VHP exhibited a high catalytic effect with benzene conversion of 76% at a combined 85.5% selectivity, toward the formation of phenol and hydroquinone achieved in six hours, under optimized reaction conditions.¹⁰¹ Among different metal-doped graphitic carbon nitride catalysts (Cu-, Fe-, V-, Co-, and Ni-mpg- C_3N_4), the vanadium-doped graphitic carbon nitride catalyst V-mpgg- C_3N_4 was found to be the most efficient.¹⁰² A bio-inspired oxo-bridged diiron(III) complex $[(\text{bpmen})_2\text{Fe}_2\text{O}(\mu\text{-O})(\mu\text{-OH})](\text{ClO}_4)_3$, bpmen = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane) also showed promising activity towards aromatic hydroxylation, with H_2O_2 and acetic acid.¹⁰³

Pyridine(Py)-modified vanadium substituted heteropoly acid ($\text{Py}_3\text{PMo}_{11}\text{V}$) with Keggin structure was applied for direct oxidation of benzene to phenol. Conventional heating gave a phenol yield of 7.8%, whereas a higher phenol yield of 24.7% and selectivity of 100% was obtained when irradiated with microwave energy.¹⁰⁴ Direct hydroxylation of benzene to phenol, using H_2O_2 as an oxidant over vanadium-containing mesoporous carbon catalysts, or molybdovanadophosphoric anion ionic liquid as a reusable catalysts for benzene oxidation to phenol by H_2O_2 , has also been reported.^{105,106}

The catalytic performance of a γ -Keggin divanadium-substituted phosphotungstate, $(\text{Bu}_4\text{N})_4\text{-}[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-O})(\mu\text{-OH})]$, has been evaluated in a selective oxidation of 1,2,4-trimethylbenzene (pseudocumene) **14** and 2-methylnaphthalene **15** with the 35% aq. hydrogen peroxide (Scheme 13). Under conditions of H_2O_2 deficiency ($\mathbf{14}/[\text{H}_2\text{O}_2] = 17\text{-}22$), oxidation of pseudocumene proceeded, with unusually high chemoselectivity and regioselectivity, producing exclusively 2,4,5-trimethylphenol **16** and 2,3,5-trimethylphenol **17** in a molar ratio of 7.3/1 and a yield of 73%, based on the oxidant. Isomeric 2,3,6-trimethylphenol was found in trace amounts. Under conditions of H_2O_2 excess ($[\text{H}_2\text{O}_2]/14 = 8$), 2,3,5-trimethyl-1,4-benzoquinone (vitamin E key intermediate) formed with 41% selectivity at 41% substrate conversion. A typical regioselectivity was also found in the oxidation of 2-methylnaphthalene **15**, which gave predominantly 6-methyl-1,4-naphthoquinone **17** rather, than isomeric **18**. The ratio between the isomers could be altered by varying the catalyst and oxidant amounts.¹⁰⁷



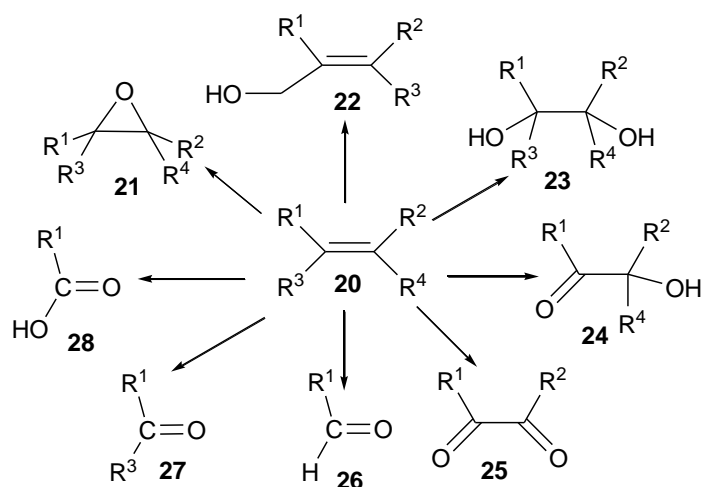
Scheme 13. Pseudocumene and 2-methylnaphthalene oxidation catalyzed by $(\text{Bu}_4\text{N})_4[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-O})(\mu\text{-OH})]$.

The alternative method for synthesis of 2-methyl-1,4-naphthoquinone, is liquid phase oxidation of 2-methylnaphthalene with H_2O_2 carried out under mild reaction conditions, over lanthanum doped MCM-41 in acetic acid as solvent. The catalyst exhibited very high substrate conversion (95.8%) and reasonable product (2-methyl-1,4-naphthoquinone) selectivity (69.3%). The catalyst can be reused twice, without losing its activity to a great extent.¹⁰⁸ Using aqueous hydrogen peroxide and palladium(II) chloride for oxidation of differently substituted benzene rings of 2-phenylpyridines, lead to phenols in up to 74% yield.¹⁰⁹

The direct oxidations of benzene to phenol and anthracenes to anthraquinones with H_2O_2 were achieved with $\text{Tp}^*\text{Cu}(\text{NCMe})[\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}]$ complexes as the catalysts.¹¹⁰ The copper(II) complexes with the bidentate ligand bis(1,4,5-trimethyl-2-imidazolyl)methane (Me_6bim), $[\text{Cu}(\text{Me}_6\text{bim})\text{X}_2]$ ($\text{X} = \text{Cl, Br}$), exhibit catalytic activity in oxidation of benzene to phenol and 1,4-benzoquinone the presence of excess H_2O_2 at room temperature in $\text{MeCN}/\text{H}_2\text{O}$ solution.¹¹¹ Catalytic activity of copper(II) 1,3,5-benzenetricarboxylate in the catalytic oxidation of benzene to phenol and hydroquinone, with hydrogen peroxide as an oxidant was reported. The corresponding oxygenates had a yield of 36.5%, and the selectivity to phenol and hydroquinone was 53.2% and 35.5%, respectively. The turnover frequency (TOF) was 35.1 h^{-1} . Moreover, water treatment protected the catalyst from decomposition due to formation of a new oxidation mode.¹¹² Selective hydroxylation of benzene to phenol has been achieved in 21% yield using H_2O_2 in the presence of a catalytic amount of the nickel complex $[\text{Ni}^{\text{II}}(\text{tepa})]^{2+}$ ($\text{tepa} = \text{tris}[2\text{-(pyridin-2-yl)ethyl}]\text{amine}$) at $60\text{ }^\circ\text{C}$.¹¹³ The selective hydroxylation of benzene to phenol was also achieved by using of $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$ ($\text{tpa} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$) incorporated in mesoporous silica-alumina as the catalyst support, which prohibits further oxidation of phenol due to the strongly acidic sites.¹¹⁴

3.3. Oxidation of alkenes

Derivatives of alkenes are one of the most important chemical products and they can be obtained by using oxidation or hydrolysis methods. Catalytic oxidation has the advantage over non-catalytic oxidation methods, in order to improve yields and selectivity and decrease environmental pollution. Oxidation of alkenes **20**, depending on the substrate and the reaction conditions, may result in the various products illustrated in Scheme 14, such as epoxides **21**, α -hydroxyalkenes **22** and diols **23**, which may be subsequently oxidized to α -hydroxyketones **24**, diketones **25** or can be cleaved into aldehydes **26**, ketones **27** or carboxylic acids **28**.



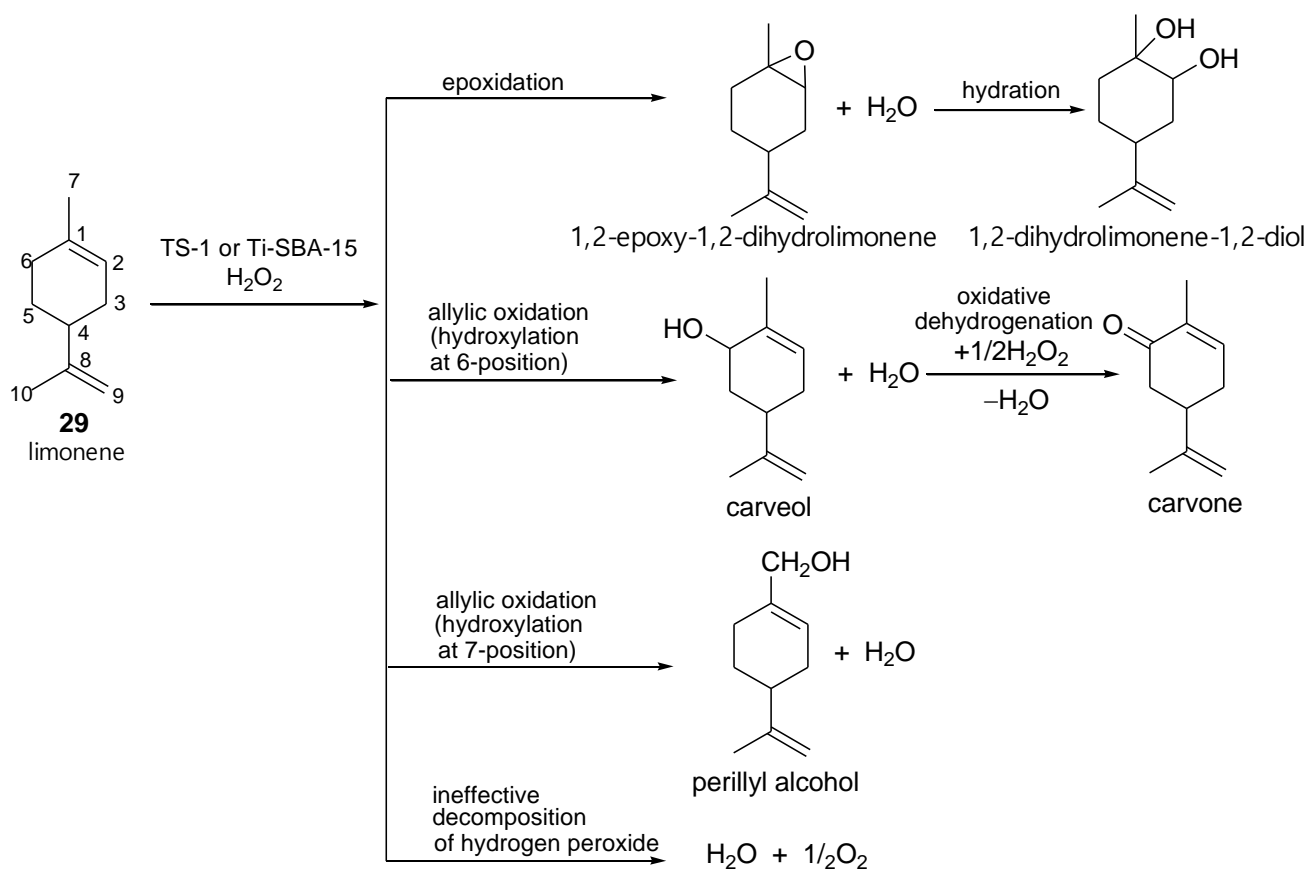
Scheme 14. Oxidation of alkenes.

During recent years, significant progress has been achieved in the oxidation of alkenes with hydrogen peroxide in the presence of titanium, manganese, copper, rhenium, iron, silver, cobalt, molybdenum, palladium and niobium compounds and complexes, carried out in liquid phase. The main challenge for researchers has been to make the oxidation reaction the most chemo-, regio- and stereoselective.¹¹⁶⁻¹¹⁹ Asymmetric epoxidation of alkenes using hydrogen peroxide as oxidant, has been a very active research field and has been investigated by many research groups. The most recent progress has been reviewed.¹²⁰

3.3.1 Epoxidation. The titanium(salalen) complex has been known as an effective catalyst for asymmetric epoxidation of enol esters. Although (*E*)-enol esters were reluctant to proceed, (*Z*)-enol esters underwent asymmetric epoxidation with H₂O₂ to give the epoxides in high yields, with high enantioselectivity ranging from 86 to 99% ee. Complete enantioselectivity was observed in the reaction of (*Z*)-3,3-dimethylbut-1-en-1-yl-4-methoxybenzoate. The obtained epoxide was readily transformed into the corresponding 1,2-diol, by reduction with lithium borohydride, without erosion of the high enantiomeric excess.^{121,122} Bryliakov and co-workers systematically studied the influence of the ligand structure on the catalytic activity and selectivity, by surveying the performance of a series of chiral salan ligands, with varying steric and electronic properties in the asymmetric epoxidation of aromatic epoxides. The results revealed, that the electronic effect controls the catalytic activity, whereas the steric effect accounts for the facial selectivity of the epoxidation.¹²³ Recently, it was reported that Ti-salan complex is able to catalyze distal selective epoxidation of conjugated dienes, even in the presence of other olefins and adjacent stereocenters. In this context, a variety of well-established methods for asymmetric epoxidation were surveyed for the regioselective epoxidation of conjugated dienes. The reaction, using Ti-salan complex or its enantiomer as catalyst, furnished the products, with complete regioselectivities in favor of the *Z*- or trisubstituted olefins over *E*-olefins. Notably, these reactions also proceeded with high diastereo- or enantio-selectivities.¹²⁴

The situation becomes more complicated when the oxidized molecule contains more active centers. An example is catalyzed oxidation of limonene **29** by titanosilicates microporous TS-1 and mesoporous Ti-SBA-15, since the substrate has both an exocyclic and an endocyclic bond. Scheme 15 shows the different possible ways of transformation, not only in the direction of 1,2-epoxylimonene and its corresponding diol, but also in the direction of other products. When TS-1 was a catalyst in this process, as a result of the electrophilic attack on the double bond (position 1–2), 1,2-epoxylimonene is formed, almost exclusively at 0 °C. 1,2-Epoxylimonene can undergo further hydration of the epoxide ring, and 1,2-dihydroxylimonene is formed. The next product of this process is carveol, formed as a result of the cyclic allylic hydrogen abstraction (allylic oxidation-hydroxylation at the 6-position). As a result of the acyclic allylic hydrogen

abstraction (allylic oxidation-hydroxylation at the 7-position), perillyl alcohol is formed. Carvone is also observed among the products of this process. This compound is formed as a result of oxidative dehydrogenation of carveol. Although, at 0 °C 1,2-epoxylimonene is a main product, at higher temperatures (40 °C, 80 °C and 120 °C) allylic oxidation products predominate over other products, mainly carveol resulting from cyclic allylic hydrogen abstraction. The other product is perillyl alcohol, which is obtained as a result of acyclic allylic hydrogen abstraction. This direction of the reaction over the TS-1 catalyst to carveol and perillyl alcohol, can be explained on the basis of the mechanism of allylic oxidation. The evidence shows that the microporous TS-1 is an active catalyst of limonene epoxidation but higher functions describing the process were obtained for the mesoporous Ti-SBA-15. Taking into account the size and the structure of the transition states for the formation of perillyl alcohol, it is proposed that its formation probably proceeds inside the narrow pores of the TS-1 catalyst. This is possible because the cyclohexene ring is flexible and it can adopt a very narrow configuration and can enter the pores. The narrow size of the pores ensures that further transformation of perillyl alcohol into the corresponding aldehyde does not occur. For the action of Ti-SBA-15 it was assumed that the reaction of allylic oxidation and oxidative dehydrogenation happen inside the wide pores, as well as on the outside surface of the catalyst.¹²⁵ The oxidation of limonene **29** to 1,2-epoxy-1,2-dihydrolimonene and 1,2-dihydrolimonene-1,2-diol, carveol, carvone and perillyl alcohol with hydrogen peroxide and *tert*-Bu hydroperoxide (TBHP) in the presence of :TS-1, TS-2, Ti-Beta, Ti-MCM-41 Ti-MWW, Fe/EuroPh catalysts were also studied.¹²⁶⁻¹²⁸

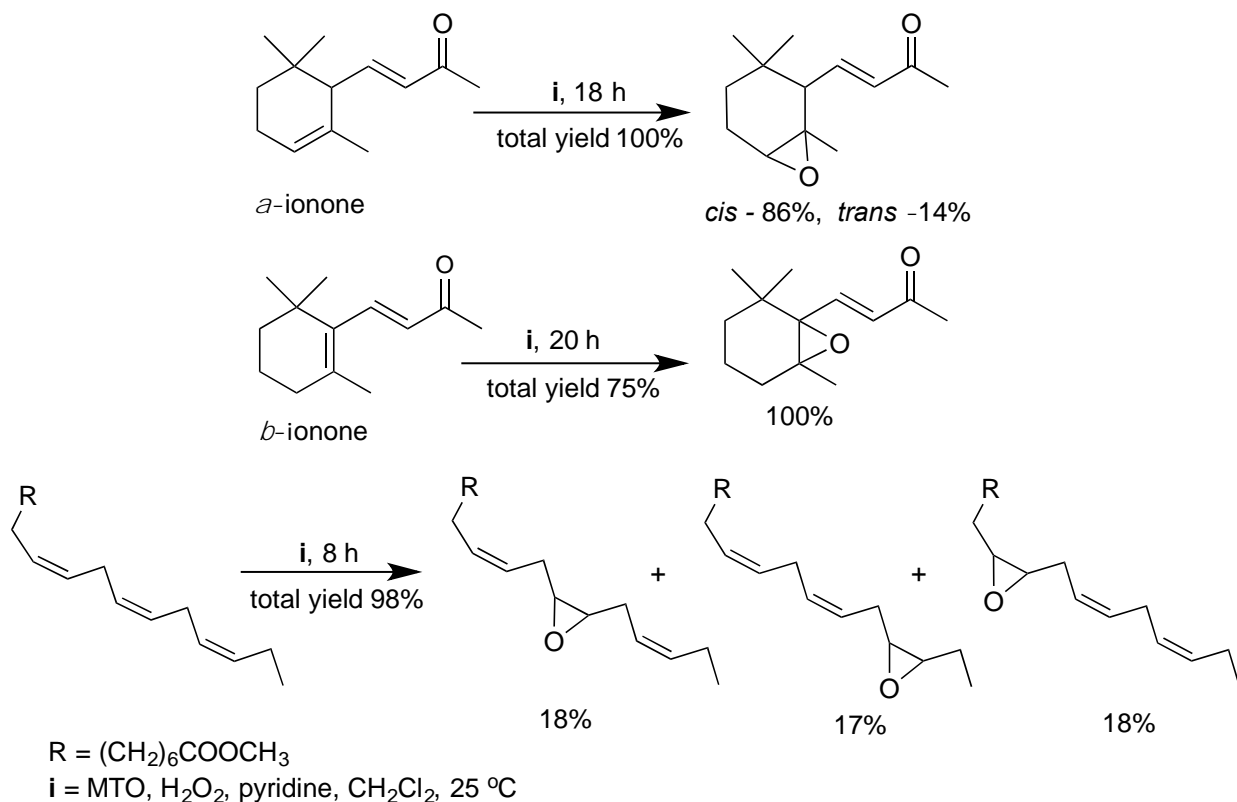


Scheme 15. Hydrogen peroxide oxidation of limonene over titanium silicates.

For epoxidation of alkenes and their derivatives, other titanium catalysts, such as Ti-YNU-1, that contains 12-membered ring interlayer pores,¹²⁹ titanosilicate MFI (a three-letter structural code among ~200 zeolite

framework codes) nanosheets of single-unit-cell thickness,¹³⁰ Ti substituted phosphotungstate [DMIM]₅PTiW₁₁O₄₀,¹³¹ Ti-SBA-15,¹³² and layered and pillared TS-1 catalysts, were also applied.¹³³

Methyltrioxorhenium (CH₃ReO₃, MTO) in the presence of H₂O₂ has proven itself as an efficient and versatile oxidation catalyst, with interesting selectivity towards natural compounds, which can be oxidized under quite mild conditions. The active species, involved in the oxygen transfer to the olefinic double bond, are probably a monoperoxo complex [MeRe(O)₂(O₂)] and a dperoxo complex [MeRe(O)(O₂)₂], obtained respectively by the addition of one or two H₂O₂ molecules to MTO. However, depending on the nature of the epoxide, a ring opening catalyzed by the Re(VII) metal center, can also occur to give 1,2-diols. Moreover, the epoxide ring opening, can be minimized by employing pyridine as a basic ligand. Epoxidation reactions of some natural compounds by MTO/H₂O₂/pyridine, lead to products of practical interest as synthons in the synthesis of fine chemicals, with the aim of assessing the parameters controlling the process. Examples are epoxidation of some natural products, having C=C bonds, of the same or different reactivity (Scheme 16).¹³⁴ Using 1-octene as a model system, under optimized conditions, a high yield and good chemoselectivity (>90 %) of epoxidation were achieved. In applications to other aromatic and aliphatic olefins, similar chemoselectivities and up to 19% enantioselectivity were obtained.¹³⁵



Scheme 16. Epoxidation of ionones and methyl linolenate with MTO/H₂O₂/pyridine system.

Schiff bases coordinate smoothly with methyltrioxorhenium (MTO), to yield the corresponding MTO-Schiff base adducts, which were used as catalysts for cyclooctene epoxidation in ionic liquids. While the urea hydrogen peroxide adduct (UHP) was used as an oxidant at room temperature, no diol byproduct formation was observed.¹³⁶ MTO, (2,6-dimethylphenyl)trioxorhenium (XTO) and benzimidazole complexes of methyltrioxorhenium were successfully employed for the epoxidation of various alkenes with H₂O₂, UHP or

t-butyl hydroperoxide.¹³⁷⁻¹³⁹ The ionic liquids were used as additives in the MTO catalyzed epoxidation and it was found that they performed well in suppressing the epoxide ring-opening reaction.¹⁴⁰ A green solvent such as diethyl carbonate was used in epoxidation reactions catalysed by oxorhenium(V) complexes [ReOCl₂(PPh₃)(L)] and [ReOCl(L)₂], with L being monoanionic bidentate phenolate-pyrazole ligands, albeit resulting in lower yields (up to 30%).¹⁴¹

A new manganese(III) complex [(N-O)₂Mn(OAc)] was synthesized using 2-(2-hydroxyphenyl)-5,6-dihydro-1,3-oxazine (N-O) as a bidentate O,N-donor. Epoxidation of alkenes to epoxides, as well as oxidation of sulfides to sulfoxides, using UHP as oxidant, resulted in high yields and selectivities.¹⁴² Manganese(II) sulfate in the presence of polyamine was reported as an efficient catalyst for epoxidation of styrene with hydrogen peroxide in 78% yield.¹⁴³ Organic carbonates, e.g. dimethyl carbonate and propylene carbonate, were used as reaction media in enantioselective epoxidation of non-functionalized alkenes, by using a series of chiral macrocyclic Mn(III) salen complexes as catalysts, with pyridine *N*-oxide as an axial base. This protocol worked effectively with UHP as oxidant, to give epoxides in high yields and ee (up to >91%).¹⁴⁴ The complex, [Mn(saldien)(N₃)], anchored on mesoporous SBA-15 produced a stable, active, and selective heterogeneous catalyst SBA15-[Mn(saldien)(N₃)] (saldien = *N,N'*-bis(salicylidene)diethylenetriamine), used for oxidation of cyclohexene (as well as cycloalkanes) in acetonitrile, with H₂O₂ as terminal oxidant. Cyclohexene was converted in 38% yield to epoxide (90%), accompanied by small amounts of enol (7%) and diol (3%).¹⁴⁵

Very recently, first example of efficient catalytic oxidation of alkenes and alcohols by a manganese(V) nitrido complex (PPh₄)₂[Mn(N)(CN)₄] using H₂O₂ as an oxidant, was reported. Epoxidation of various alkenes was investigated in the presence and absence of acetic acid. In the absence of acetic acid, 100% conversion could be achieved for electron-rich alkenes, with excellent yields of epoxide products. On the other hand, for terminal alkenes such as 1-octene, the reaction rate and yield were lower. The epoxidation of *cis*-2-heptene, *cis*-β-methylstyrene, and *trans*-β-methylstyrene, were highly stereospecific; 100% yields of the corresponding epoxides could be obtained and no epimerized products could be detected. The rate of alkene epoxidation is greatly enhanced by acetic acid. When di-substituted and tri-substituted alkenes were used as substrates, the reactions were complete within five minutes. Longer reaction times, up to one hour, were required for the epoxidation of terminal alkenes.¹⁴⁶

Polyoxomolybdates, generated *in situ* by treating a carboxylic acid-functionalized ionic liquid with aqueous sodium molybdate, showed a good performance in the epoxidation reaction (e.g. cyclooctene) and can be reused several times without significant loss of activity.¹⁴⁷

An efficient and highly selective heterogeneous catalyst was developed by immobilization of a manganese complex on an inorganic support. Mn(II) has been anchored on the surface of functionalized silica by means of N,O-coordination to the covalently Si-O bound, modified salicylaldiminato Schiff base ligand. Cycloalkenes and linear alkenes were oxidized efficiently to their corresponding epoxides with 83-98% conversion and 87-100% selectivity, in the presence of this catalyst. Furthermore, this material was shown to be very active catalyst in clean epoxidation reactions using combined oxidant of aqueous hydrogen peroxide and acetonitrile in the presence of aqueous NaHCO₃. The obtained results showed that this catalytic system was a robust and stable heterogeneous catalyst which can be recovered quantitatively by simple filtration and reused multiple times without loss of its activity.¹⁴⁸ These same authors introduced a new catalytic system, based on an immobilized imidazole-manganese-porphyrin (Mn(Porph)) for the oxidation of olefins. Merrifield resin (MR) and functionalized silica gel (SG) were chosen as supports. The results indicate, that the Mn(Porph)-MR system shows high reaction rates, high efficiency with hydrogen peroxide as oxidant and good recyclability up to four times, without a dramatic loss in the catalytic efficiency.¹⁴⁹ In another article, they also presented a

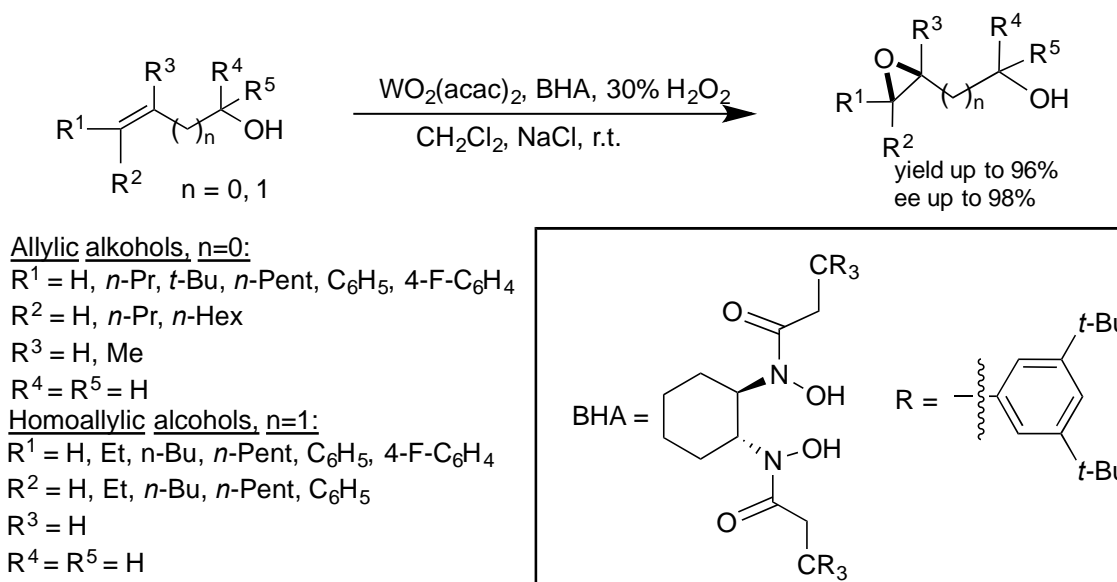
manganese-substituted polyoxomolybdate tetrabutylammonium (TBA) salt $\text{TBA}_4[\text{PMo}_{11}\text{Mn}(\text{H}_2\text{O})_{39}]\cdot 2\text{H}_2\text{O}$, which was used as the catalyst in the homogeneous oxidation of *cis*-cyclooctene, cyclohexene, styrene and geraniol with H_2O_2 in acetonitrile. Oxidation of *cis*-cyclooctene and geraniol gave only epoxides; cyclohexane-1,2-diol was the main product for cyclohexene; styrene was preferentially oxidized to benzaldehyde.¹⁵⁰

The potassium salt of PW_{11}Zn and the new composite $\text{PW}_{11}\text{Zn-APTES@SiO}_2$, were shown to be versatile catalysts for the oxidation of alkenes using H_2O_2 as the oxidant and acetonitrile as the solvent. Cyclohexene was oxidized to epoxide, geraniol to 2,3-epoxygeraniol while styrene gave benzaldehyde accompanied with 2-hydroxy-1-phenylethanone and benzoic acid as minor products.¹⁵¹ Iron catalysts, bearing tridentate non-heme ligands for use in the epoxidation of alkenes with hydrogen peroxide as the oxidant, were also developed.¹⁵² Nb-SiO₂ catalysts displayed an excellent performance in the epoxidation of limonene.¹⁵³

The synthesis and characterization of new $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-MgO}$ catalysts and their application in oxidative dehydrogenation and epoxidation reactions, were reported.¹⁵⁴ Oxovanadium(IV) complex (VOL-Y) of a Schiff base ligand, derived from 2,4-dihydroxyacetophenone and 2,2'-dimethylpropanediamine, was encapsulated in the nanopores of zeolite-Y. The encapsulated complex catalyzed the oxidation of various olefins, using hydrogen peroxide in good yield. Under the optimized reaction conditions, in the presence of VOL-Y, 86% conversion of cyclooctene with 100% selectivity for epoxide was observed.¹⁵⁵ New mononuclear oxovanadium(IV) complexes $[\text{VO}(\text{acac})(\text{R-BIAN})]\text{Cl}$ (BIAN = 1,2-bis{(R-phenyl)imino}acenaphthene) were successfully used for the catalytic oxidation of alkenes such as cyclohexene, *cis*-cyclooctene, and styrene, with both *tert*-butylhydroperoxide or H_2O_2 as the oxidant.¹⁵⁶

Alkylaminophosphazenes (RPN) are efficient and tuneable phase-transfer agents for environmentally benign biphasic oxidation with hydrogen peroxide, catalyzed by polyoxometalates (POMs). Substituent groups on the phosphazene ring, can be varied to modify the phase-transfer efficiency of RPN for use in water-organic two-phase systems. Active phosphazene-polyoxometalate aggregates that self-assemble *in situ* from RPN and Keggin POMs, such as $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$, were found to be efficient and recyclable catalysts for the epoxidation.¹⁵⁷ The Keggin and Wells–Dawson sandwich-type POMs, with various transition metals in the central belts, proved to be active catalysts for the oxidation of cyclooctene and cyclohexene with H_2O_2 . Under the reaction conditions, Wells–Dawson-type POMs were less active than Keggin ones. Zn- and Fe-substituted POMs, of both types, gave higher conversions. With tetra-*n*-butylammonium salts of $[\text{Zn}_4(\text{PW}_9\text{O}_{34})_2]^{10-}$, $[\text{Fe}_4(\text{PW}_9\text{O}_{34})_2]^{6-}$, $[\text{Zn}_4(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ and $[\text{Fe}_4(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$, high to excellent conversions of cyclooctene and cyclohexene were obtained. The main products were epoxides and the minor ones α -alcohols or α -ketones.¹⁵⁸

Over the past few decades the use of peroxotungstates as catalysts for epoxidation with H_2O_2 has attracted much attention as a result of their high capability for oxygen transfer and low activity for disproportionation of H_2O_2 . Recently, the first tungsten-catalyzed asymmetric epoxidation of allylic and homoallylic alcohols was developed (Scheme 17). With catalysis by the W–bishydroxamic acid (BHA) system, primary, secondary, and tertiary allylic, as well as homoallylic alcohols, were successfully employed as precursors in asymmetric epoxidation reactions to furnish chiral products, generally with excellent enantioselectivities. Notably, the reactions were performed under air, in most cases at room temperature, and requiring no anhydrous solvent or preparation of the metal-complex catalyst prior to the catalytic process. Moreover, this method demonstrates good chemoselectivity for primary alcohols over secondary and tertiary alcohols. For instance, two farnesol derivatives bearing three olefin and two alcohol moieties were reacted as precursors of the epoxidation reaction; they provided the corresponding products with almost complete regioselectivity in favor of oxidation of the C=C double bond which is closer to the primary alcohol. This method seems very promising for use in the late stages of synthesis of complex molecules.¹⁵⁹



Scheme 17. Tungsten catalyzed asymmetric epoxidation of allylic and homoallylic alcohols.

Four new molybdenum and tungsten complexes bearing tetradentate tripodal amino bisphenolate ligands with either hydroxyethylene or hydroxyglycolene substituents have been described and tested as catalysts in the epoxidation of cyclooctene under eco-friendly conditions, using an aqueous solution of H_2O_2 as the oxidant and dimethyl carbonate (DMC) as solvent or neat conditions as substitute for chlorinated solvents. Molybdenum complexes showed good catalytic activity using H_2O_2 without added solvent, and tungsten complexes showed very high activity.¹⁶⁰ Composites of $[\gamma\text{-H}_2\text{PV}_2\text{W}_{10}\text{O}_{40}]^{3-}$ and $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ supported on Fe_2O_3 acted as effective and reusable heterogeneous catalysts for selective oxidation with aqueous hydrogen peroxide. In the presence of $\text{PV}_2\text{-SiW}_{12}/\text{Fe}_2\text{O}_3$, various kinds of organic substrates such as alkenes, sulfides, arenes, and alkanes were selectively converted into the corresponding oxygenated products in moderate to high yields. For example 1-octene gave epoxide in 85% preparative yield and cyclooctene was oxidized to epoxide in 89% yield while selectivity was above 99% in both reactions. The catalysts could be reused at least three times without appreciable loss of their catalytic performance.¹⁶¹ The catalytic behavior in olefin epoxidation of a one-dimensional tungsten oxide/2,2'-bipyridine hybrid material was also recently reported.¹⁶²

Iron-catalyzed asymmetric epoxidation is attractive owing to the availability, low cost, and low toxicity of iron salts. Generally, the iron catalysts for asymmetric epoxidation can be classified into two categories: porphyrin- and non-porphyrin iron complexes. The oxidant used in these catalytic systems has generally been iodosyl benzene. In 2012, Simonneux and his co-workers developed a series of chiral iron-porphyrins, which were able to promote asymmetric epoxidation using hydrogen peroxide as oxidant. Notably, the sulfonated Halterman iron-porphyrin is water soluble and thus under its catalysis the epoxidation can be conducted under aqueous conditions. However, the substrate scope of these reactions is narrow and includes only styrene derivatives and 1,2-dihydronaphthalene. Furthermore, the products are afforded mostly with only moderately good enantioselectivities.^{163,164} Tetradentate nitrogen-containing ligands, which have electronic properties that resemble those of porphyrin, also proved to be efficient catalysts for the Fe-catalyzed asymmetric epoxidation of olefins. For instance, a chiral Fe-aminopyridine catalyst was developed, which was capable of promoting highly enantioselective epoxidation of diverse olefins with aqueous hydrogen peroxide as oxidant. Furthermore, the authors also discovered that the enantioselectivity of this process increased with

growing steric demand of acidic additives. A plausible mechanism was also proposed.¹⁶⁵ The catalytic behaviour of the Fe–aminopyridine complex was significantly improved by introducing a dimethylamino moiety to the pyridine rings. The addition of a catalytic amount of a carboxylic acid as cocatalyst, improved both yields and enantioselectivities of the epoxidation reaction through synergistical cooperation with the iron complex leading to more efficient O–O bond cleavage and the formation of epoxidizing species. After careful screening of a variety of carboxylic acids, Ibuprofen turned out to be the best coligand. This new epoxidation method demonstrates a broad substrate scope including various enones and *cis*- β -substituted styrenes.¹⁶⁶ Recently, amino acids were employed as synergistic coligands for the Fe–aminopyridine-complex-catalyzed epoxidation of α -substituted styrenes, which are challenging substrates for asymmetric epoxidation. Generally, under optimum conditions, the epoxide products were obtained in high enantiomeric excess. The authors' new observations revealed that the substrate spectrum of a catalytic system can be simply expanded through variation of coligands instead of onerous development of novel ligands.¹⁶⁷ Sun *et al.* developed a Fe–aminobenzimidazole complex, which proved to be an efficient catalyst for H₂O₂-mediated enantioselective epoxidation of chalcones, furnishing the products in most cases with high enantioselectivities.¹⁶⁸ Mn- and Fe-catalyzed asymmetric epoxidations are similar in terms of the ligands employed, the substrate scope, and the reaction mechanism. The use of hydrogen peroxide as oxidant in Mn-catalyzed epoxidation was reviewed recently by Krishnan *et al.*¹⁶⁹ Being similar to iron, the manganese–porphyrin complexes were found to be able to catalyze the asymmetric epoxidation of unfunctionalized olefins with aqueous hydrogen peroxide as oxidant but the substrate scope was relatively narrow and the level of the asymmetric induction was only moderate.¹⁷⁰ In 2011, Bryliakov *et al.* discovered that a Mn complex with a tetradentate aminopyridine ligand featuring a cyclohexanediamine scaffold was an efficient catalyst for the enantioselective epoxidation of olefins using aqueous hydrogen peroxide as the terminal oxidant and a large excess amount of acetic acid as additive, although the products were obtained in lower enantioselectivities. The same research group also developed a chiral tetradentate aminopyridine ligand based on a bis-pyrrolidine structure, which turned out to be a good ligand for the Mn-catalyzed H₂O₂-mediated asymmetric epoxidation of electron-deficient olefins, thereby yielding the products in moderate-to-good enantioselectivities. Furthermore, the authors also observed that the use of a sterically demanding carboxylic acid instead of acetic acid as additive improved the enantioselectivities of this Mn-catalyzed epoxidation reaction.¹⁷¹ Later, Costas *et al.* also reported a chiral bis-pyrrolidine-based ligand bearing modified pyridine rings as ligand arms for the Mn-catalyzed asymmetric epoxidation. In this case, the products were provided in high yields albeit with low to moderate enantioselectivities.¹⁷² In 2012, Sun *et al.* described a Mn-catalyzed asymmetric epoxidation by employing a tetradentate *N*-ligand containing chiral bis-pyrrolidine and benzimidazole moieties. Under the optimum reaction conditions, high to excellent enantioselectivities were achieved when using chalcones and *cis*-disubstituted olefins as substrates. In contrast, relatively poor facial control was observed in the cases of terminal, *cis*-disubstituted olefins, and α,β -unsaturated esters.¹⁷³ It was discovered independently that introduction of electron-donating substituents to the pyridine rings of the aminopyridine ligands led to the enhancement of both the efficiency and enantioselectivities of the Mn-catalyzed epoxidation with hydrogen peroxide as terminal oxidant. In the cases of α,β -unsaturated carbonyl compounds and chromenes as substrates the products were obtained with high enantioselectivities. Furthermore, study of the use of the Mn complex for the diastereoselective epoxidation of unsaturated steroids revealed that the formation of β -epoxides was favored when using the Mn catalysts.^{174,175} In 2013, Gao *et al.* developed a porphyrin-inspired chiral Mn–amino-oxazoline complex and applied it successfully in the asymmetric epoxidation of a variety of olefins using aqueous hydrogen peroxide as the terminal oxidant. In the cases of *trans*-stilbene and cyclic

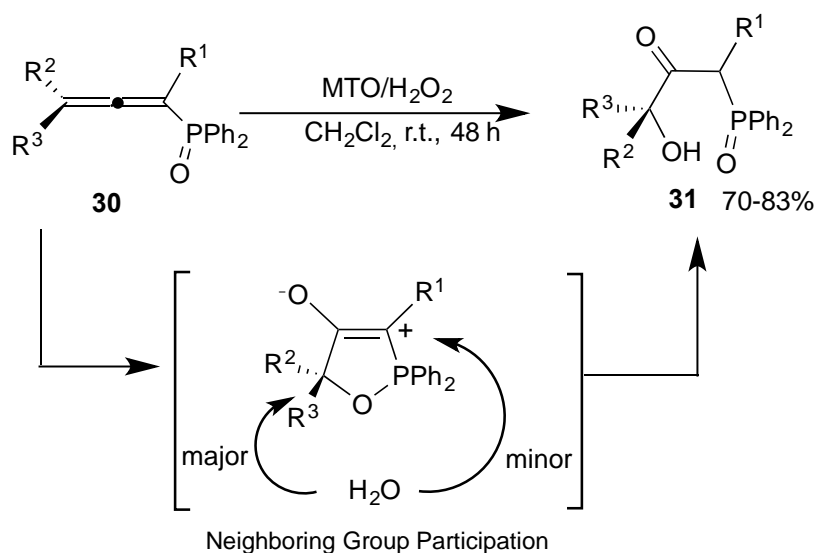
olefins such as indene, dihydronaphthalenes, as well as chromenes as substrates, the products were furnished in good to excellent enantiomeric excess. Moreover, the authors also observed an increase in enantioselectivity when the reactions were conducted in the presence of an acidic additive.^{176,177} New chiral manganese complexes of N4 ligands derived from 2-acetylpyridine were prepared and used as catalysts in the enantioselective epoxidation of olefins, using H₂O₂ as an oxidant to give epoxides, with excellent conversions (up to 99%) and enantiomeric excess (up to 88%) within 1 h at 0 °C.¹⁷⁸

The Mn 1,4,7-trimethyl-1,4,7-triazacyclononane dimers were activated by carboxylate-containing solids for cyclooctene epoxidation/dihydroxylation with H₂O₂ at 0 °C. Dihydroxylation selectivities are a function of the carboxylate employed as well as the nature of the other groups on the solid cocatalyst surface. SiO₂ grafted with propionate groups gave ~50% *cis*-diol selectivity, but further modification with alkyl or perfluoroalkyl silanes increased *cis*-diol selectivity up to ~60%. Dihydroxylation selectivity is also ~60% for SiO₂ grafted with benzoate or ~70% for terephthalic acid chemisorbed on TiO₂.¹⁷⁹ It has been demonstrated that chiral manganese aminopyridine complexes [LMn^{II}(OTf)₂] are able to epoxidize olefins with excellent enantioselectivities (up to 99% ee, several examples) with various terminal oxidants (H₂O₂, alkyl hydroperoxides, peroxyacids, and iodolylarenes). The mechanisms of enantioselective olefin epoxidations on aminopyridine manganese(II) complexes [LMn^{II}(OTf)₂] with different oxidants was also considered.¹⁸⁰

The catalytic property of phosphomolybdic acid (PMA) functionalized knitting aryl network polymer (KAP) was investigated for the selective oxidation of cyclooctene and other olefins with H₂O₂ as oxidant. When ethyl acetate was used as reaction medium, the catalyst gave a 78.6% conversion of cyclooctene with nearly 100% selectivity for epoxide. Moreover, this catalyst shows high activity and selectivity for epoxide formation for a variety of olefins, and it can be reused for several times without obvious loss of activity. Also, the PMA/KAP catalytical system can even oxidize the relative inert terminal olefins of 1-hexene and 1-octene to their corresponding epoxides.¹⁸¹

Gold-nanoparticle-containing mesoporous monoliths were subsequently investigated in flow reactors for the oxidation of cyclohexene to a mixture of oxygenates: cyclohexene oxide (56.7%), 2-cyclohexen-1-one (22.7%) and 2-cyclohexen-1-ol (20.6%). The conversion of cyclohexene was low (2.7%), and in some experiments *tert*-butyl hydroperoxide was a better oxidant than hydrogen peroxide.¹⁸²

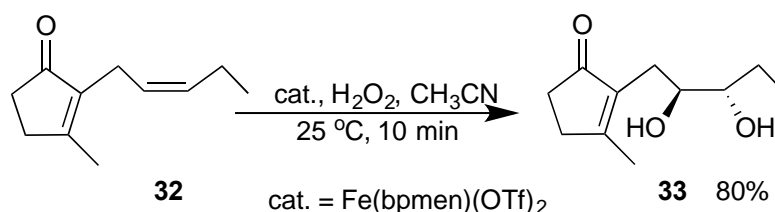
3.3.2. Hydroxylation, aminohydroxylation and aminochlorination. Current methodology for the catalytic *cis*-dihydroxylation of alkenes with preparative significance in organic synthesis is mainly focused on osmium and ruthenium compounds. For the synthesis of the 1,2-diols, *cis*-1,2-dihydroxylation of alkenes catalyzed by osmium(VIII) tetroxide (OsO₄) is a powerful method. However, OsO₄ is quite toxic due to its highly volatile and sublimable nature. Thus, the development of alternative catalysts for *cis*-1,2-dihydroxylation of alkenes has been highly challenging. A simple protocol that uses a nitrogen-based tetradentate ligand, tris(2-pyridylmethyl)amine (tpa), for an osmium center and [Os^{III}(OH)(H₂O)(L-N₄Me₂)](PF₆)₂ (L-N₄Me₂ = *N,N'*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane) as catalysts and H₂O₂ as terminal oxidant for *cis*-1,2-dihydroxylation of alkenes was presented. Unfunctionalized (or aliphatic) alkenes and alkenes/styrenes containing electron-withdrawing groups were selectively oxidized to the corresponding vicinal diols in good to excellent yields (46-99%). For the dihydroxylation of cyclohexene, the catalyst amounts can be reduced to 0.01 mol% to achieve a very high turnover no. of 5500. The active oxidant is hydroperoxide identified as the Os^V(O)(OH) species, which is formed via the hydroperoxide adduct, an Os^{III}(OOH) species.^{183,184}



Scheme 18. Oxidation of 1,2-allenyl diphenyl phosphine oxide with H₂O₂/MTO.

For the first time, methyltrioxorhenium (MTO) has been applied as a catalyst for the dihydroxylation of functionalized allenes **30** in the presence of hydrogen peroxide as the oxidant. The regioselectivities turn out to be well controlled, affording β -carbonyl- γ -hydroxyl diphenyl phosphine oxides **31** as the only product (Scheme 18). The axial chirality of optically active allenes can also be nicely transferred to the chirality center of the products. A possible mechanism, proceeding via regioselective epoxidation of the electron-rich carbon-carbon double bond, a subsequent intermolecular nucleophilic attack of a water molecule on the in situ formed epoxide via neighboring group participation (NGP), followed by a rearrangement has been proposed as the major reaction pathway.¹⁸⁵

Accordingly, the development of alternative catalysts for the 1,2-dihydroxylation of alkenes with hydrogen peroxide catalysed by iron complexes has been recently reported. It has been seen that the most effective non-heme iron catalysts are those possessing nitrogen-based tripodal or linear tetradentate ligands, such that two *cis* labile sites available for coordination with exogenous ligands become available. In an investigation of the dihydroxylation of alkenes, the iron complexes Fe(bpmen)(OTf)₂ (bpmen: bispicolyl-*N,N*-methylethylenediamine) and Fe(tpa)(OTf)₂ (tpa: tripicolylamine. OTf: trifluoromethanesulfonate) were applied as the catalysts. A broad set of substrates was oxidized and in most cases the reaction was regio- and stereo-selective. The example shown in Scheme 19 is *trans*-dihydroxylation of (*Z*)-jasmone **32** to diol **33**.¹⁸⁶



Scheme 19. *trans*-Dihydroxylation of (*Z*)-jasmone.

Iron(III) phthalocyanine complexes were employed for the first time as mild and efficient Lewis acid catalysts in the selective oxidation of cyclohexene to cyclohexane-1,2-diol. It was found that the catalyst

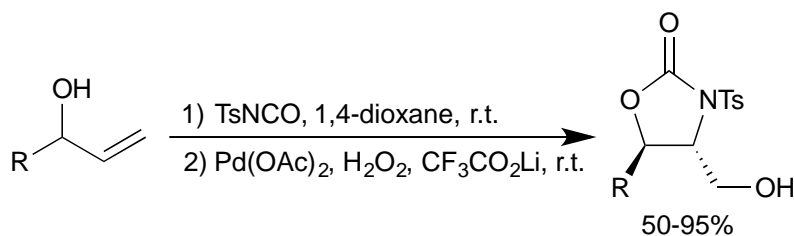
FePcOTf shows excellent conversion and moderate selectivity relative to other iron(III) phthalocyanine complexes.¹⁸⁷ Simple $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was demonstrated to be able to catalyze the oxidation of monoterpenes by hydrogen peroxide in methanol. In these reactions, α - and β -pinene were preferentially oxidized to allylic ethers (i.e., myrtenol methyl ether).¹⁸⁸ For oxidation of cyclohexene with hydrogen peroxide the selectivity for α -hydroxylation is favoured and cyclohex-2-en-1-ol is produced when iron(II) and cobalt(II) phthalocyanines are catalysts.¹⁸⁹

It was demonstrated that mesoporous ZrO_2 -POMs composites based phosphotungstate and Ti-substituted phosphotungstates composites exhibited catalytic activity for the oxidation of cyclohexene with H_2O_2 as oxidant resulting in mixtures of oxidation products mainly cyclohexen-3-one, cyclohexen-3-ol and cyclohexan-1,2-diol.¹⁹⁰ The direct formation of α -alkoxyalcohols from the corresponding olefin through the oxidation of cyclohexene with hydrogen peroxide is catalyzed by commercially available molybdenum catalysts. 2-Methoxycyclohexanol was obtained with high yields and 99% selectivity by using as catalyst the $[\text{C}_4\text{mim}]_4[\text{Mo}_8\text{O}_{26}]$ complex (C_4mim = 1-butyl-3-methylimidazolium).¹⁹¹

Oxidation of terminal alkenes was smoothly catalyzed by a recyclable and environmentally friendly tungsten catalytic system: $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_3[\text{PW}_4\text{O}_{16}]/\text{H}_2\text{O}_2/\text{formic acid}$. This new catalytic system is not only capable of catalyzing oxidation of terminal alkenes with a phase-transfer character, but also under solvent-free conditions, avoiding the use of chlorinated solvents. Many different kinds of terminal alkenes could be converted to the corresponding 1,2-diols of high purity in high yields. The catalyst could be easily separated and reused after reaction.¹⁹²

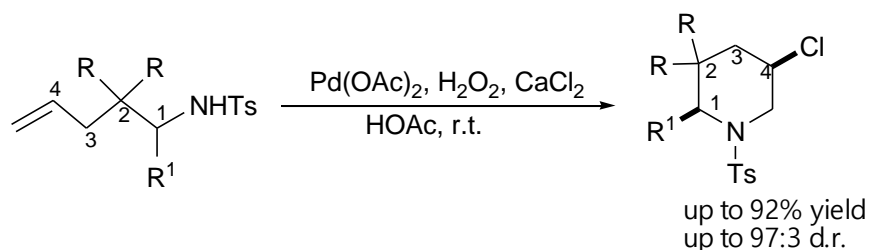
Allylic C-H bond oxidation, resulted in the formation of unsaturated α -alcohol or α -ketone, was demonstrated on cyclohexene and α -pinene. Oxidation of α -pinene with hydrogen peroxide catalyzed with $\text{VO}(\text{OAc})_2$ gave verbenon as the major product (45.9% selectivity at 82.9% conversion) and formation of campholenic aldehyde, myrtenal, verbenol and epoxy-pinane as byproducts was also observed.¹⁹³ The α -pinene conversion was close to 25%, verbenone being the major product using M41S type nano-structured material with Cu content ca. 7% in the reaction of α -pinene oxidation with H_2O_2 . The reaction has a high practical value because verbenone can provide a starting point for the synthesis of taxol, an important therapeutic agent and as an intermediate for manufacture of pesticides and in the flavour industry. Oxidation of cyclohexene leads to cyclohex-2-en-1-ol and cyclohex-2-en-1-one. The reaction path involves a first stage where the interaction $\text{Cu-Me}(x)$ catalyst with H_2O_2 yields $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ species. Then $\cdot\text{OH}$ attacks the olefin with formation of allylic oxidation products such as cyclohex-2-en-1-ol and cyclohex-2-en-1-one or verbenol and verbenone. It displays preferential attack on the C-H bond over C=C bond and promotes the allylic oxidation pathway while epoxidation is unfavored.¹⁹⁴

A palladium diacetate - catalyzed intramolecular aminohydroxylation (Scheme 20) and aminoacetoxylation of alkenes was developed, in which H_2O_2 was applied as the sole oxidant. A variety of related products could be successfully obtained with good yields and excellent diastereoselectivities, which directly derived from oxidative cleavage of an alkyl C-Pd bond by H_2O_2 . Facile transformation of these products provided a powerful tool for the synthesis of 2-amino-1,3-diols and 3-hydroxy amino acids as well as β -acetoxyated piperidines. Preliminary mechanistic studies revealed that a main nucleophilic attack by water ($\text{S}_{\text{N}}2$ type) at the high-valent Pd center contributes to the final C-O(H) bond formation.^{195,196}



Scheme 20. Pd-catalyzed intramolecular aminohydroxylation of alkenes.

A highly selective Pd-catalyzed oxidative intramolecular chloroamination of unactivated alkenes has been developed by using an environmentally benign catalytic system, in which H_2O_2 was used as oxidant and CaCl_2 as chlorine source. A variety of chlorinated piperidine compounds were obtained with good regio- and diastereoselectivities (Scheme 21). A possible catalytic cycle involves Pd(II)-catalyzed *trans*-aminopalladation of the alkene by nitrogen nucleophilic attack at the terminal 6-*endo* carbon then generated Pd(II) intermediate undergoes an oxidation by H_2O_2 . Direct reductive elimination from the Pd(IV) intermediate generates the C-Cl bond.¹⁹⁷



Scheme 21. Intramolecular chloroamination of alkenes.

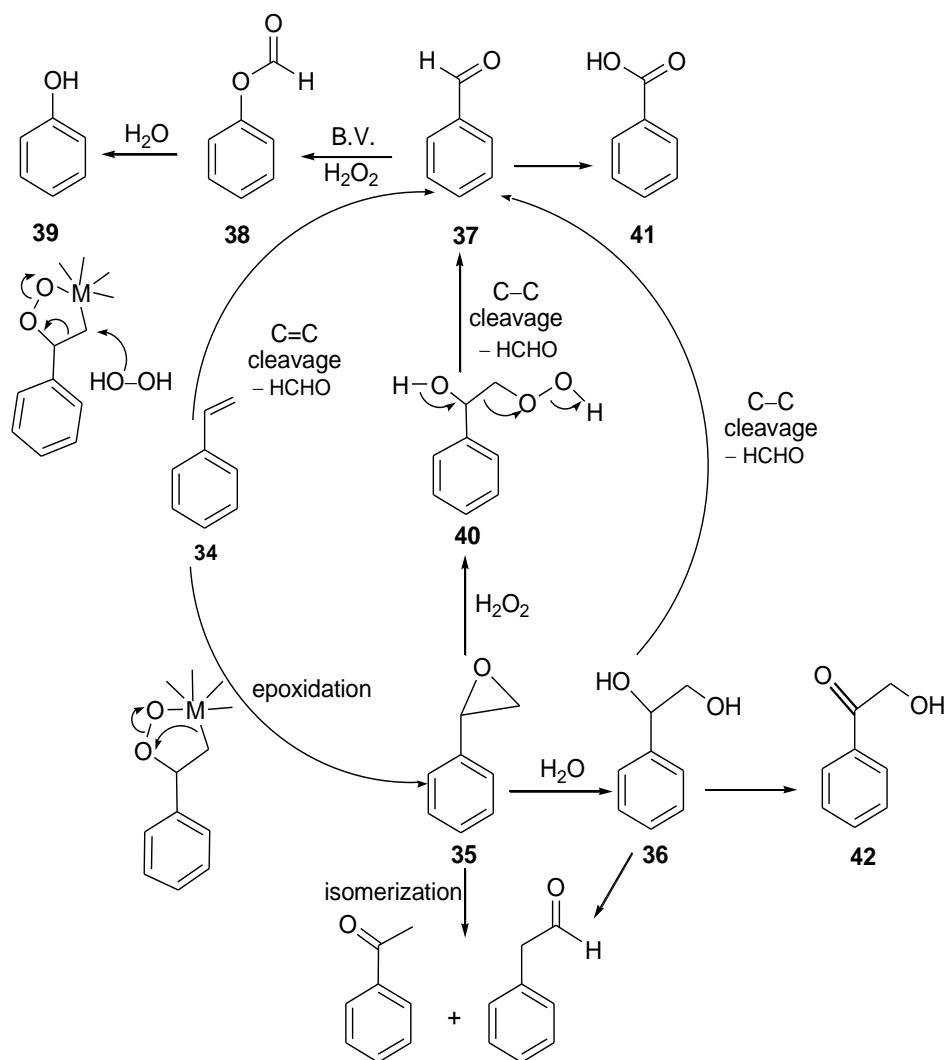
The effect of 6-methyl-substituted di(2-pyridyl)methanesulfonate (Me-dpms) and di(2-pyridyl)ketone (dpk) ligands on the selectivity oxidation of ethylene with H_2O_2 in acetic acid solution has been explored. The results indicated that the palladium complexes supported by dpk and Me-dpms ligands are efficient catalysts for selective oxidation of ethylene with 30% aqueous H_2O_2 to glycol acetates. Glycol acetates could be obtained in up to 90% yield based on H_2O_2 and with 95% selectivity under mild conditions (1 atm pressure of ethylene, 20 °C), with 1 mol% catalyst loading. By contrast, the reaction catalyzed by $\text{Pd}(\text{OAc})_2$ alone, is inefficient in terms of utilization of H_2O_2 and is unselective, producing mostly vinyl acetate and acetaldehyde in low yield. The most active catalyst, developed in this work, consists of a mixture of palladium acetate and derived dpk and Me-dpms complexes.¹⁹⁸

3.3.3. Oxidation of styrenes. The particular case of styrene oxidation is of considerable interest for academic research and also for industry due to the important products that can be obtained, such as styrene oxide, benzaldehyde or phenylacetaldehyde. Like the oxidation of other alkenes, the initial step of polyoxometalate catalyzed oxidation of the C=C bond in styrene **34** and other vinylbenzenes is formation of an epoxide **35** (Scheme 21). This can be selectively obtained by hydrogen peroxide in the presence of phosphomolybdic acid supported on ionic liquid modified MCM-41¹⁹⁹ or *cis*-dioxomolybdenum(VI) Schiff base complex.²⁰⁰ Oxidation of styrene with H_2O_2 in presence of NaHCO_3 catalyzed by polystyrene (PS), supported PS-[$\text{Mo}^{\text{VI}}\text{O}_2(\text{hap-iah})(\text{MeOH})$], obtained by the condensation of equimolar amounts of *ortho*-hydroxy acetophenone (hap) and indole-3-acetic hydrazide (iah), gave mainly styrene oxide as a major product.²⁰¹ In a

report on the catalytic properties of symmetrical and unsymmetrical imidazolium-containing manganese porphyrins in hydrogen peroxide oxidation of styrene the high conversion of the substrate (80-100%) and high selectivity in forming the epoxide (above 80%) was noted.¹⁴⁸ Other reports on the epoxidation of styrene have been discussed in Sections 2.1^{28,33} and 3.3.1^{143,146,150,163, 164, 166, 167,168}

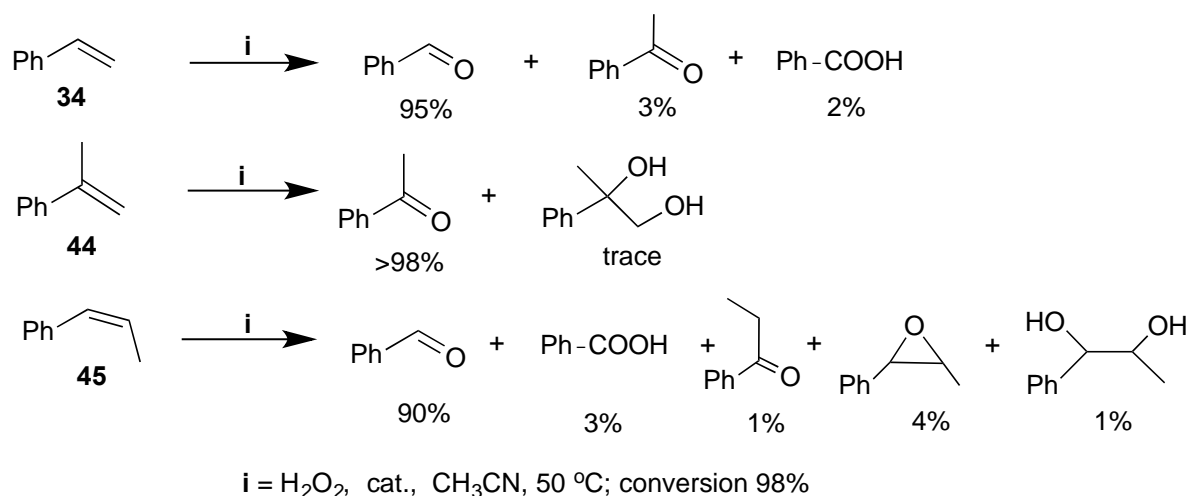
In most cases, the unstable oxirane ring of epoxides immediately undergoes subsequent reactions, and various compounds, shown in Scheme 22 are formed as final products. From a study on the oxidation of styrene catalyzed with polyoxometalates (BW11M, PW11M, SiW11M; M = Mn, Co, Fe), it was concluded that styrene oxide **35** and diol **36** are potential intermediates in the formation of benzaldehyde. Benzaldehyde can be formed by C–C cleavage of the diol (after hydrolysis of the epoxide) and by oxirane ring opening by direct action of H₂O₂, which results in the formation of formaldehyde and benzaldehyde. Formation of the epoxide is described as the formation of an intermediate peroxide or hydroperoxide complex with the catalyst, in which H₂O₂ is coordinated to a metal centre of the POM. The oxygen transfer from the bonded peroxide to styrene may occur by different mechanisms, namely, through the formation of a 5-membered cyclic intermediate involving a metal centre (M = W, Fe, Mn, Co). Probably this intermediate could also react with a H₂O₂ molecule, resulting in the direct formation of benzaldehyde. This third pathway for the C=C cleavage is suggested since, the epoxide and the diol may not be responsible for all the benzaldehyde formed. Phenol was also detected in a very small amount. The formation of phenol **39** is well established in the Baeyer–Villiger oxidation of aromatic aldehyde **37** via the corresponding formate ester **38**, which may be hydrolyzed to the corresponding phenol.²⁰² As reported by Hulea and Dimitriu, the formation of benzaldehyde (major product) takes place via two different mechanisms. (1) In the presence H₂O₂ styrene **34** is oxidized to styrene epoxide **35**, which transforms into a hydroxyl-hydroperoxy-ethyl benzene intermediate **40** when H₂O₂ attacks it as a nucleophile. Cleavage of hydroxyl-hydroperoxystyrene produces both benzaldehyde and formaldehyde. (2) Direct oxidative cleavage of the C=C bond of styrene via a radical mechanism, yields both benzaldehyde **37** and formaldehyde. Benzoic acid **41** is one of three minor products, which is expected to form from benzaldehyde **37** through oxidation. Another minor product is 2-hydroxyacetophenone **42** formed from 1-phenylethane-1,2-diol **36**, which is believed to be produced through hydrolysis of styrene epoxide **35** making use of the H₂O present in aqueous 30% H₂O₂.²⁰³

Catalysts incorporating tungsten in a silica matrix, composed of isolated [WO₄]²⁻ species, isolated tungsten species or low oligomeric tungsten oxide species and crystalline WO₃ species, were tested in the liquid phase oxidation of styrene using H₂O₂ as oxidant. Benzaldehyde was obtained as the major product with 100% selectivity.²⁰⁴ Vanadyl(IV)acetylacetonate anchored SBA-15 catalyst, was reported as a versatile, recyclable, and reusable solid catalyst for the oxidative cleavage of C=C bonds of styrene and its derivatives to the corresponding carbonyl compounds at up to 38–95% conversion levels with 63–99% selectivity of cleavage products under mild reaction conditions particularly at atmospheric pressure, room temperature, with aqueous H₂O₂ oxidant.²⁰⁵ The catalytic performances of spinel Mg-Cu ferrite complex oxides such as Mg_{0.5}Cu_{0.5}Fe₂O₄ were evaluated as catalysts in oxidations of styrene in water. Styrene conversion at 22% and 84% selectivity for benzaldehyde was obtained at 80 °C for a nine hour reaction. The catalyst can be magnetically separated and reused without loss of activity.²⁰⁶ The Ti-phenyl@SiO₂ with Si/Ti molar ratio of two showed the best catalytic performance for the oxidation of styrene, with 92% conversion and 99% selectivity towards benzaldehyde.²⁰⁷ A porous carbon layer formed from carbon-coated titania (C@TiO₂) exhibited high catalytic activity towards hydrogen peroxide oxidation of styrene to a mixture of benzaldehyde and phenylacetaldehyde.²⁰⁸ Other transition metal complexes, namely Fe^{III}₂MO(OOCCH₃)₆(C₆H₅N)(H₂O)₂, M=Fe, Cr,



Scheme 22. Oxidation of styrene **34**.

Mn, Ni;²⁰⁹ zinc phthalocyanine supported on multi-walled carbon nanotubes,²¹⁰ *N*-heterocyclic carbene metal carbonyl complexes based on 1-[2-(pyrazol-1-yl)phenyl]imidazole were also reported as catalysts for the selective conversion of styrene to benzaldehyde.²¹¹ A μ -oxido divanadium compound [(VOL)₂(μ -O)] with an aliphatic hydrazone ligand LH₂ = (*E*)-*N*'-(1-(2-hydroxyphenyl)ethylidene)acetohydrazide was used for the oxidation of styrene in the presence of H₂O₂. A conversion of 99.7% and selectivity of 88% for benzaldehyde formation and a turnover no. of 1354 was found under the most favorable reaction conditions.²¹² The catalytic properties of novel oxovanadium(IV) complexes having different donor ligands covalently anchored on SBA-15, in the H₂O₂ promoted oxidation of conjugated olefins like styrene **34**, α -methylstyrene **44** and *cis* β -methylstyrene **45** were investigated, in terms of activity, selectivity and recyclability. The main product was benzaldehyde or benzophenone accompanied by small amounts of other compounds as shown in Scheme 23.²¹³



Scheme 23. Oxidation of styrenes with oxovanadium(IV) complexes.

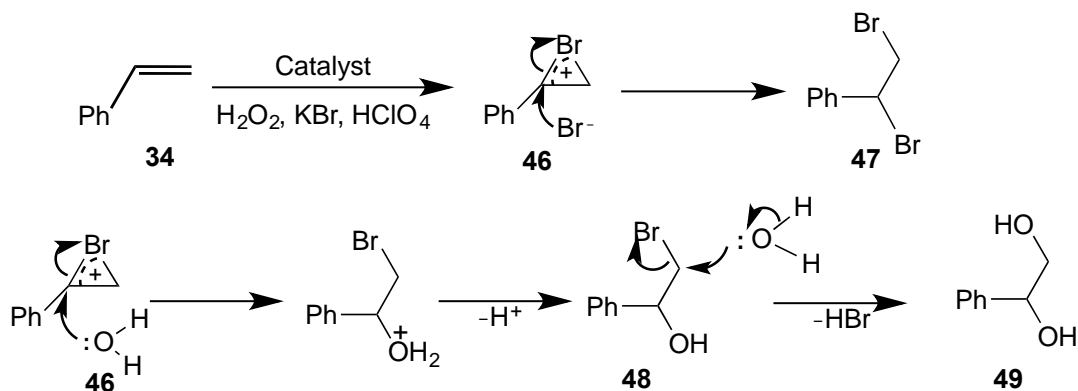
Ferrocene and ferrocenyl-modified periodic mesoporous organosilica (PMO) were employed in the catalytic oxidation of styrene at 55 °C using either hydrogen peroxide or *tert*-butylhydroperoxide as oxidant. The main reaction product was always benzaldehyde, together with other products including styrene oxide, benzoic acid and 2-hydroxyacetophenone. Using a styrene : H₂O₂ molar ratio of 1 : 5, the highest PhCHO yields after 24 hours were 65% (85% selectivity) for ferrocene and 34% (83% selectivity) for the modified PMO. The modified PMO could be recovered and reused, albeit with a fall in catalytic activity due to partial metal leaching during the first catalytic run.²¹⁴ A novel visible light photocatalyst of iron(II) bipyridine complex, encapsulated within an NaY zeolite was successfully used as the catalyst for selective oxygenation of styrene with high turnover (1800) and high benzaldehyde selectivity (86%). This photocatalyst was also effective for the oxidation of other olefins, such as 4-cyanostyrene, 4-methoxystyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*- β -methylstyrene, α -methylstyrene, triphenylethylene, 1-octene, 2-octene, cyclohexene and cyclooctene, to the corresponding aldehydes, ketones or epoxides.²¹⁵ The selective styrene oxidation to benzaldehyde was also studied over Cr-ZSM-5 zeolite. The effects of various reaction parameters such as reaction time, catalyst mass, styrene/hydrogen peroxide molar ratio, solvent nature and reaction temperature were evaluated.²¹⁶

Among oxidovanadium(IV)-exchanged zeolites-Y, the most active catalyst was the zeolite abbreviated as [V^{IV}O(pydx-en)]-Y. Oxidations of styrene, cyclohexene and methyl phenyl sulfide were investigated using these complexes as catalysts. Under the optimized reaction conditions for [V^{IV}O(pydx-en)]-Y a maximum of 85.5% conversion of styrene was obtained in six hours of reaction time. The selectivity of the various products followed the order: benzaldehyde > 1-phenylethane-1,2-diol > benzoic acid > phenyl acetaldehyde. A maximum conversion of 96% was achieved for cyclohexene. The selectivity of the various products was: cyclohex-2-en-1-one > cyclohex-2-en-1-ol > cyclohexane-1,2-diol.²¹⁷ Very high selectivity toward cyclohex-2-en-1-ol was achieved when Fe-bipyridine complexes encapsulated into Y-type zeolite Na-Y ([Fe(bpy)₃]²⁺@Y) were used as the catalysts.²¹⁸

Polymer and non-polymer-grafted dioxidomolybdenum(VI) complex [Mo^{VI}O₂(sal-iah)(MeOH)] having donor ligand H₂sal-iah (derived from salicylaldehyde and indole-3-acetic hydrazide), catalyzes the oxidative bromination by H₂O₂ of styrene and *trans*-stilbene. Under the optimized reaction conditions, the oxidative bromination of styrene gave 96% conversion in two hours, where 2-bromo-1-phenylethane-1-ol **48** (45%) and 1-phenylethane-1,2-diol **49** (51.2%) are the main products, and 1,2-dibromo-1-phenylethane **47** (2.0%) is the

minor product. Oxidative bromination of *trans*-stilbene gave 96% conversion in two hours, with 2,3-diphenyloxirane (*trans*-stilbene oxide), 1,2-dibromo-1,2-diphenylethane and 2-bromo-1,2-diphenylethanol as the products.

The peroxide $[\text{Mo}^{\text{VI}}\text{O}(\text{O}_2)]^{2+}$ intermediate species formed under reaction conditions, may oxidize the bromide (to Br_2 , Br_3^- and/or HOBr), which may react with styrene to give bromonium ion **46** as intermediate. The attack of nucleophile Br^- on the α -carbon of the intermediate gives 1,2-dibromo-1-phenylethane **47** while attack by H_2O gives 2-bromo-1-phenylethanol-1-ol **48**. The nucleophile H_2O may further attack at the α -carbon of 2-bromo-1-phenylethanol-1-ol to give 1-phenylethane-1,2-diol **49** (Scheme 24). The observed poor selectivity of dibromo product **47** is possibly due to its fast sequential conversion into the mono-bromo derivative **48**, which in turn forms the diol **49**. The conversion of monobromo derivative alone under the optimized reaction conditions was also tested and the formation of 1-phenylethane-1,2-diol was observed. The presence of acid in the aqueous phase possibly promotes the protonation of the peroxido moiety and the presence of KBr is essential to obtain reasonable amounts of brominated products.²¹⁹ Sodium bicarbonate-assisted oxidation, by H_2O_2 , of styrene and cyclohexene using polymer grafted dioxidomolybdenum(VI) complex as a catalyst was also reported.²²⁰

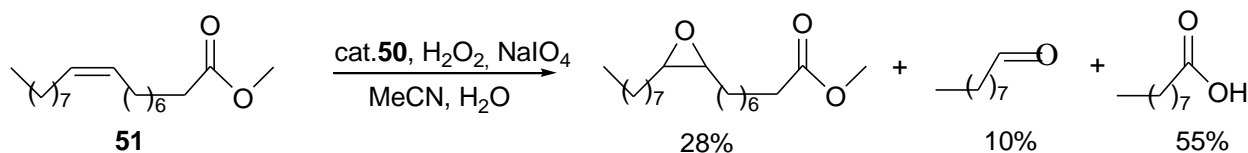


Scheme 24. Proposed mechanism for the formation of three main products (**47-49**), after the bromonium ion is formed by action of catalytically generated HOBr on styrene.

3.3.4 Oxidative cleavage of alkenes. Oxidative cleavage of alkenes is one of the most prevalent reactions in organic synthesis. The two main oxidative cleavage pathways can be summarized: conversion of alkenes to vicinal diols and subsequent cleavage with NaIO_4 or other oxidants and ozonolysis, in which the olefin is directly cleaved into functionalized products depending on work-up conditions. Ozonolysis is quite reliable, but has always had major safety concerns. Ozone gas is highly toxic and its generation requires specialized equipment. Examples of alternative reactions to ozonolysis include Noyori's cleavage of olefins to carboxylic acids with hydrogen peroxide and Na_2WO_4 , Ranu's $\text{InCl}_3/t\text{-BuOOH}$ cleavage of alkenes and alkynes to carboxylic acids, and several other transition metal-mediated protocols.^{222,223} More recently, oxidative cleavage of aryl and alkyl olefins to the corresponding aldehydes, catalyzed by OsO_4 , employing H_2O_2 as the terminal oxidant was reported. Aryl olefins were cleaved in good to excellent yields regardless of arene electronics. Alkyl olefins are cleaved in moderate to good yields for di- and tri-substituted alkenes.²²⁴

The first Fe-based catalytic system for the oxidative cleavage of unsaturated fatty acids and esters to carboxylic acids use a system comprising $[\text{Fe}(\text{OTf})_2(6\text{-Me-PyTACN})]$ **50**, (6-Me-PyTACN = 1-[(6-methyl-2-pyridyl)methyl]-4,7-dimethyl-1,4,7-triazacyclononane, OTf = trifluoromethanesulfonate anion) as the catalyst

either with a combination of hydrogen peroxide and NaIO₄ or exclusively with NaIO₄ as the oxidant, and operates at 0 °C or ambient temperature (Scheme 25). Under these conditions, methyl oleate **51** was converted in a one-pot procedure into 50-55% of both nonanoic and azelaic acid, together with some epoxide and aldehyde intermediates as byproducts. This catalytic system provides an alternative to the industrial ozonolysis of oleic acid and to catalytic Ru- and Os-based systems for the oxidative cleavage of unsaturated fatty acids and esters.²²⁵



Scheme 25. Oxidative cleavage of methyl oleate with complex **50** as catalyst and H₂O₂/NaIO₄.

For the one-pot oxidative cleavage of internal alkenes to aldehydes, the nonheme iron complex [Fe(OTf)₂(mix-bppb)] (bppb=N,N'-bis(2-picolyl)-2,2'-bipyrrrolidine) was used as catalyst.²²⁶ A green synthesis of adipic acid, in 82% yield, from cyclohexene oxidized by H₂O₂-silicotungstic acid under ultrasonication was reported.²²⁷ In the same reaction a novel silica-functionalized ammonium tungstate interphase catalyst successfully used.²²⁸ A new synthesis strategy for the preparation of metallic silver nanoparticles (AgNPs) supported on tungsten oxide (WO₃) nanorods with diameters between 40 and 60 nm in the presence of a cationic surfactant cetyltrimethylammonium bromide (CTAB) was developed. The catalyst was very effective in liquid phase hydrogen peroxide oxidation of cyclohexene to adipic acid. A cyclohexene conversion of >99.9% with an adipic acid selectivity of >94% was achieved with a very high turnover frequency.²²⁹ Ligated Pd(II) complexes have been studied for the catalytic oxidation of terminal olefins to their corresponding methyl ketones using hydrogen peroxide as the terminal oxidant.²³⁰ A series of quaternary ammonium perrhenate 3-hexyl-1-methylimidazolium hydrogen sulfate ([Hmim]HSO₄) composite ionic liquids were prepared and used both as catalyst and solvent in oxidation of cyclooctene to suberic acid in the presence of hydrogen peroxide as a green oxidant. The yield of suberic acid under the mild conditions was from good to high.²³¹

2-Pyridylmethyl pendant armed ethylene side-bridged cyclam complexes of copper(II), iron(II), and manganese(II) have been prepared, characterized, and screened for oxidation catalysis. Using these complexes and hydrogen peroxide as terminal oxidant 1,4-cyclohexadiene was dehydrogenated to benzene in 71% yield (conversion 86%).²³²

4. Conclusions

In this review an attempt has been made to summarize progress in the exploitation of the metal-containing catalysts for hydrogen peroxide oxidations of C-H, C-C and C=C bonds, made in recent years, based on the literature from 2011 to early 2016. Different compounds and complexes mainly of iron, vanadium, copper, manganese, rhenium, vanadium, molybdenum, titanium, tungsten, palladium, osmium, zirconium, chromium, silver, cobalt and also bismuth and aluminum are indicated as oxygen-transfer agents while 30% aqueous hydrogen peroxide is a stoichiometric oxidant. Most of the described oxidant/catalyst systems are ecologically friendly reagents particularly these using the iron and manganese and vanadium compounds, and complexes or heterogenous systems where catalyst is easily separated from

the reaction products and can be reused without loss of the activity. They are convenient for modern organic synthesis and have been used for various groups of organic compounds among them for hydrocarbons. The review covers recent advances in their application for oxidation of C-H, C-C and C=C bonds in alkanes, arenes and nonfunctionalized as well as in functionalized alkenes. The most important reactions are hydroxylation of benzene rings, oxyfunctionalization of the methyl and methylene groups in alkanes, cycloalkanes and alkylarenes toward carbonyl and carboxylic group as well as in epoxidation, α -hydroxylation, 1,2-dihydroxylation and other reactions of alkenes. Based on the described reactions, new methodologies for synthesis of alcohols, phenols, aldehydes, ketones, epoxides and carboxylic acids are indicated. Different mechanisms for the oxygen-transfer processes, heterolytic or homolytic, and the stereochemistry of some important reactions are discussed and their scope and limitations are indicated.

It is hoped that this review can serve as a valuable critical overview of the area and the contribution helps in encouraging further research in this field. I would like to apologize to anyone who finds my description of her or his work inadequate or whose work has been omitted.

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Author's Biography



Halina Wójtowicz-Młochowska was born in Kielce, Poland. She obtained her M.Sc. degree in Chemistry at Wrocław University of Technology, Poland and completed her Ph.D studies in the Institute of Organic and Physical Chemistry at the same University in 1976. She moved to Antwerp University to take up a postdoctoral position with Prof. Achiel Hammers in 1993. Subsequently she has worked in the organic research group in the Institute of Organic Chemistry, Biochemistry, and Biotechnology at Wrocław University of Technology. Her scientific interest has been concentrated on the chemistry of nitrogen, sulfur, oxygen and selenium heterocycles, biomimetic applications of oxidation processes with hydroperoxides in synthetic practice, and evaluation of the biological activity of selenium compounds. Recently the area of her research interest has been the design and study on synthetic application of metal and non-metal catalysts for electron- and oxygen transfer processes.