**“Recent advances in the catalytic oxidation of alkene and alkane substrates using immobilized manganese complexes with nitrogen containing ligands”**

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# Introduction

The development of sustainable methods for the catalytic oxidation of alkene and alkane [[1](#_ENREF_1)] substrates is an important scientific challenge with significant technological potential [[2](#_ENREF_2)]. In particular, the hydroxylation of alkanes and the *cis*-dihydroxylation and epoxidation of alkenes are important reactions as they allow for the transformation of simple hydrocarbon substrates into high value fine chemicals (Scheme 1) [[3](#_ENREF_3)].



**Scheme 1**. Representation of the important catalytic oxidations targeted herein.

Moreover, there is the additional pressure that if the technological potential of the chemistries is to be realised in an industrial setting, they must be environmentally friendly, relying on atom economic and non-toxic reagents, and must operate under mild conditions [[4](#_ENREF_4)]. Nature provides us with a blueprint on which to base model systems, where there exist many naturally occurring metalloenzymes which activate dioxygen using transition metals, such as iron and manganese [[5](#_ENREF_5)], and lead to the formation of products with high regio-and stereocontrol, but often with high substrate specificity. One of the best known and understood metalloenzymes, which activates dioxygen in this manner is cytochrome P450. It has been proposed that iron(IV)–oxo porphyrin π-cation radical intermediates act as active complexes in these processes [[6](#_ENREF_6)]. Although a vast number of ‘enzyme-like’ systems e.g. mimicking heme and non-heme iron and manganese oxygenases in selective hydroxylation [[7-9](#_ENREF_7)], alkene epoxidation [[10-13](#_ENREF_10)] and *cis*-dihydroxylation [[14-16](#_ENREF_14)] have been reported, the development of environmentally friendly systems capable of performing these transformations with high levels of activity, efficiency, chemo-, regio- and stereoselectivity remains a major challenge. Moreover, the synthesis of the target catalysts sometimes requires numerous synthetic steps, in many cases involving expensive reagents or purification processes, and the final products are obtained with low overall yield. The catalysts can often only be used in one catalytic reaction, due to their decomposition when harmful intermediates are formed. Due to these complications, one of the major obstacles that scientists have to overcome is the recycling and reuse of catalysts, as well the prevention of their unwanted decomposition [[17](#_ENREF_17)] during oxidation reactions. Partially [[18](#_ENREF_18)], these disadvantages could be eliminated by immobilization of catalysts on solid supports [[19-22](#_ENREF_19)]. In general, catalyst heterogenisation (i) can allow for easy leaching of products, by-products and excess reagents by simple solvent washing, which also reduces possible degradation of the catalyst during work-up of crude reaction mixtures; (ii) can provide the opportunity for catalyst re-use in multiple synthetic steps over long periods; and (iii) could change i.e. increase, decrease, invert catalyst selectivity and productivity.

The aforementioned advantages of immobilization have had a huge impact and in recent years immobilized catalysis has become an important field ~~of high importance~~ in the synthesis of high value molecules. Hence, there have been increasing numbers of reviews about the application of immobilized catalysts in organic transformations [[23-31](#_ENREF_23)]. The previous reviews are focused on the oxidation of hydrocarbons by various terminal oxidants, in the presence of numerous metallocatalysts e.g. manganese, iron, copper, vanadium complexes with acac, porphyrins and Schiff base ligands immobilized on different supports, e.g. inorganic materials of different structure and surface morphology, polymer supports, metal-organic framework as well as focusing on various types of immobilization e.g. covalent or noncovalent heterogenisation.

In this review, recent (2000-2017) catalytic applications of immobilized manganese complexes with nitrogen containing ligands such as Schiff base ligands, including salens, porphyrins and amine ligands, mainly TMTACN (1,4,7-trimethyl-1,4,7-triazacyclononane), are summarised. Since many reviews have been published relating to the type of immobilization (e.g. covalent [[32](#_ENREF_32)] and noncovalent [[33](#_ENREF_33)] immobilization) and support type (e.g. mesoporous materials [[34-36](#_ENREF_34)], polymeric materials [[37](#_ENREF_37), [38](#_ENREF_38)], nanostructured supports [[39](#_ENREF_39)], MOF [[27](#_ENREF_27), [40-43](#_ENREF_40)], graphene [[44](#_ENREF_44)]) these issues are not presented here, however, the arrangement of this article has been based on the ligand structure as well as chemical composition (type) of the solid support and bonding/interaction to/with these materials. Typically, the materials have been grouped in inorganic supports with demarcated silica-based surfaces, organic and hybrid i.e. organic-inorganic supports, and then through the type of immobilization i.e. covalent bonding (coordination bonding through the metal center) and non-covalent bonding including encapsulation, physical adsorption and electrostatic interaction.

# Immobilized Manganese Complexes with Schiff-Base Ligands

The best-known examples of Schiff-base complexes are based on salen ligands. The first salen-metal complex was reported in 1933 [[45](#_ENREF_45)], and the term “salen” is now widely used to describe a group of bisimine compounds having a structure derived from the *N*,*N*’-bis(salicylidine)ethylenediamine. Although the imine or Schiff base group is susceptible to acid-catalyzed hydrolysis, its stability increases upon formation of the salen-metal complex and can consequently be used in aqueous media. Ligands synthesised from 3,5-*di*-*tert*-butyl-salicylaldehyde and optically pure cyclohexane-1,2-diamine are arguably the most popular and widely used in asymmetric catalytic applications. Manganese complexes of this ligand were first reported as asymmetric epoxidation catalysts by Jacobsen and Katsuki [[46](#_ENREF_46)] in 1990 [[47](#_ENREF_47), [48](#_ENREF_48)] and have been widely applied in the asymmetric epoxidation of certain alkene substrates and are broadly known as either Jacobsen’s catalyst or the Jacobsen-Katsuki catalyst (Fig. 2.1) [[49-52](#_ENREF_49)]. Many other complexes of the ligand and transition metals (e.g. Cr, Co, V, Cu, Ti, Ru, Pd, Au, Zn and Al) have been investigated and have been shown to possess catalytic activity in many different reaction types, including hydrolytic epoxide ring-opening, cyclopropanations, aziridinations, selective hydrogenations, carbonyl cyanosilylation, hetero-Diels-Alder, imine or aldehyde additions [[53-55](#_ENREF_53)], and as a result of its wide efficacy in asymmetric catalysis the salen ligand is now considered to be a priviliged ligand [[55](#_ENREF_55), [56](#_ENREF_56)]. Consequently, considerable effort has been devoted to the development of different methodologies to transform homogeneous metallosalen complexes into reusable heterogeneous catalysts. Numerous strategies for immobilizing metallosalen complexes have been reported, including covalent anchoring on mesoporous materials or polymers, their encapsulation in zeolites, immobilization through ion-exchange process on layered double hydroxides (LDH). The application of heterogenised metallosalens published up to 2006 has been summarised in an earlier review “*Chiral Salen Complexes:  An Overview to Recoverable and Reusable Homogeneous and Heterogeneous Catalysts*” **by Baleizão and Garcia** [[25](#_ENREF_25)].



**Figure 2.1.** The structures of Jacobsen’s catalyst, **2.1**, and Katsuki’s catalytic systems, **2.2**, for the epoxidation of certain alkene substrates.

## Manganese Complexes with Schiff-Base Ligands Immobilized on Inorganic Supports

### Manganese Complexes with Schiff-Base Ligands Immobilized on Silica-Based Supports via Covalent Bonding (C-C, C-N, C-S, C-O)

Reports of covalent immobilization of salen-metal complxes onto inorganic supports can be grouped into two main categories: i) linkage through functionalization of the salen aromatic ring or ii) immobilization via modification of the diamine used to derive the imine nitrogens.

#### Immobilization by a sulfide group

|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Ref. |
| *m*CPBA | NaOCl |
| **2.3** | conv 75%,  ee 47% | conv 71%, ee 51% | [57] |
| **2.4** (achiral) | - | yield 81.4% | [58] |
| **2.5** (achiral) | - | yield 50.1% | [58] |
| **2.6** | - | conv 71.8%, ee 24.4% | [59] |
| **2.7** | - | conv 76.9%, ee 41.2% | [59] |
| **2.8** | conv 78.2%,  ee 36.8% | conv 81.8%, ee 30% | [60] |
| **2.9** | conv 60.1%,  ee 40.7% | conv 90.3%, ee 51.9% | [60] |

**Figure 2.2**. The structures and catalytic activity of manganese(III) salen complexes immobilized via sulfide linkages onto mesoporous silica with best conversion (conv) or reported yield.

The manganese(III) salen complexes **2.3-2.9** (Fig. 2.2) were covalently immobilized on mesoporous silica through functionalization of the salen aromatic ring by a sulfide linkage and tested in the epoxidation reaction of alkenes with NaOCl or *m*-CPBA as the terminal oxidant, with or without an axial base such as NMO and PPNO. Complex **2.3** [[57](#_ENREF_57)] was immobilized on the mercaptopropyltrimethoxysilane-functionalized mesoporous materials (MCM-41), complexes **2.4** and **2.5** [[58](#_ENREF_58)] (Fig. 2.2) were anchored onto mesoporous propylthiol group-functionalized silica with 2D hexagonal *p6mm* (S-SiO2-2Dhex and S-PMO-2Dhex) and 3D interconnected sponge-like structures (S-SiO2-3Dint), whereas catalysts **2.6**-**2.9** [[59-61](#_ENREF_59)] were embedded on series of MCM-41 and MCM-48 with different pore sizes. A summary of the the best results obtained with catalysts **2.3-2.9** instyrene oxidation are presented in Fig. 2.2. Complexes **2.4** and **2.5** [[58](#_ENREF_58)] exhibited high selectivity (*ca*. 100%) for styrene oxide and good to moderate yields. Catalysts **2.3** and **2.9** were found to be the most effective for the epoxidation of styrene using *m*CPBA and NaOCl (Fig. 2.2). The activity of the catalyst and enantioselectivity of the epoxidation reaction were closely correlated with the pore sizes of the heterogeneous catalysts **2.6**-**2.9** [[59-61](#_ENREF_59)]. The catalysts grafted onto MCM-41 and MCM-48 with bigger pores exhibited higher efficiency than those attached on supports with smaller pores. In addition, heterogeneous catalyst **2.3** [[57](#_ENREF_57)] provided lower conversions than its homogeneous analogue ~~but~~ with comparable enantioselectivities, but **2.8**-**2.9** [[60](#_ENREF_60), [61](#_ENREF_61)] yielded much lower enantioselectivities and conversions than its homogeneous counterpart. Reuse of the most active systems was investigated, and it was shown to be relatively stable with small decerases in yield and catalyst loading being observed after the third run.

#### Immobilization by an amine group

Several examples of catalyst immobilization via amine groups without modification of the imine nitrogen of the catalyst have been reported and selected examples will be referred to in the following section.



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Catalyst** | Styrene oxide (the best conv/yield) | | | Ref. |
| *m*CPBA | NaOCl | TBHP |
| **2.10** | conv >99%  ee 49% | - | - | [62] |
| **2.11** | conv 50%  select 91.2%  ee 4.4% | conv 75.6%  select 39.5%  ee 44.7% | - | [63] |
| **2.13** | - | yield >99%  ee 70% | - | [65] |
| **2.14** | conv 59%  ee 49% | - | - | [66] |
| **2.15** | conv 35%  ee 32% | - | - | [67] |
| **2.16** | conv 10%  ee 2% | - | - | [67] |
| **2.19** (achiral) | - | - | conv 95%  select 57% | [70] |

**Figure 2.3.** Structures and the activities of manganese(III) Schiff base complexes covalently immobilized by nitrogen.

As was the case for catalysts **2.6**-**2.9** [[59-61](#_ENREF_59)], the catalytic ability of Mn(salen) complex **2.10** (Fig. 2.3) [[62](#_ENREF_62)] anchored onmesoporous MCM-41 and MCM-48 materials with different pore sizes, tested in alkene oxidation using *m*-CPBA/NMO, were firmly correlated with the pore sizes of the supports, and the use of catalysts supported on mesoporous surface possessing larger pores exhibited higher substrate conversions and enantioselectivities. Moreover, in some reactions with the hetereogenous catalysts, better results were obtained than with their homogenous analogues. In the presence of complex **2.11** [[63](#_ENREF_63)] (Fig. 2.3) grafted on MCM-41 much ~~better~~ higher ee of styrene oxide was obtained using NaOCl/PyNO than *m*-CPBA/NMO, hovewer the epoxide selectivity was higher when *m*-CPBA/NMO system was applied. Catalyst recycling experiments showed leaching of manganese during reuse, an erosion of selectivity and enantiomeric excess. The efficiency of structurally similar catalyst **2.12** immobilized on amine modified Davisil silica gel was explored in the epoxidation of some monoterpenes, including (+)-limonene (Fig. 2.4) [[64](#_ENREF_64)], but the diastereomeric control of the reactions resulted from the chirality of the substrate rather than that of the homogeneous or heterogeneous catalysts.



**Figure 2.4.** The possible products obtained from (*R*)-(+)-limonene: (i) *cis*-1,2-limonene oxide, (ii) *trans*-1,2-limonene oxide, (iii) *cis*-8,9-limonene oxide, (iv) *trans*-8,9-limonene oxide, (v) diepoxide, (vi) carveol, (vii) carvone.

Another effective epoxidation system was achieved using chiral dimeric Mn(salen) complex anchored on mesoporous silica through a melamine-piperazine linker (**2.13**, Fig. 2.3) and NaOCl/PyNO [[65](#_ENREF_65)]. The supported catalyst exhibited satisfactory activity and ability to be reused, which resulted in product formation with high yield, together with good enantioselectivity, and turnover frequency (TOF).

Although, the oxidation of alkenes such as styrene and its analogues using complexes **2.14**-**2.16** [[66](#_ENREF_66), [67](#_ENREF_67)] (Fig.2.3) covalently anchored on MCM-48 and *m*-CPBA/NMO gave noticeably lower conversions than in the presence of homogeneous catalysts, in some cases using the heterogenous catalyst provided significant increase of ee. In addition,the presence of bulky substituents on the aromatic ring of the ligand had an important influence on catalyst efficiency, for example in the presence of catalyst **2.16** devoid of substituents, styrene oxide was formed with low ee (only 2%), whereas in the presence of **2.15** with *tert*-butyl groups, it was much higherand reached48% ee [[67](#_ENREF_67)]. In addition to a mesoporous silica MCM-41 and MCM-48, Mn(salen) complex **2.17** (Fig. 2.3) was covalently grafted onto silylated quartz substrates [[68](#_ENREF_68)] and successfully used in the enantioselective epoxidation of the selected substrate, 6-cyano-2,2-dimethyl-chromene, in the presence of NaOCl. More significantly after ten catalytic cycles the activity remained at the same level and no catalyst leaching was observed, thus allowing continuous recycling.

Other terminal oxidants including hydrogen peroxide and TBHP were also applied in hydrocarbon oxidation using catalysts immobilized on silica through nitrogen incorporated into the ligand. For example, the catalyst **2.18** (L = N3) [[69](#_ENREF_69)] (Fig. 2.3) immobilized on mesoporous silica SBA-15 was tested in the oxidation of selected cycloalkenes and cycloalkanes using hydrogen peroxide, and similar selectivities and conversions were obtained under hetero- and homogeneous conditions, but in some cases reversed selectivity occured. Complex **2.19** was also anchored onto SBA-15 [[70](#_ENREF_70)] which catalysed styrene epoxidation with TBHP as the terminal oxidant, however styrene oxide was formed with moderate selectivity.



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best result) | Ref. | **Catalyst** | Styrene oxide (the best result) | Ref. |
| *m*CPBA | *m*CPBA |
| **2.20** | TON 19, TOF 5, ee 1% | [71] | **2.21** | TON 24, TOF 6, ee 1% | [71] |

**Figure 2.5.** Other *N*-linked manganese(III) Schiff base complexes

The catalyst **2.20** immobilized on modified hexagonal mesoporous silica (HMS) through the functionalised pyrrolidine part of the complex, and catalyst **2.21** anchored via a modified salicylaldehyde were applied in styrene and -methylstyrene epoxidation with *m*-CPBA and NaOCl, but the activity of the heterogeneous catalysts **2.20**, **2.21** and their non-immobilized analogues were considerably lower than those obtained in reactions in the presence of original Jacobsen’s catalyst [[71](#_ENREF_71)].



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | Ref. | **Catalyst** | Styrene oxide (the best conv/yield) | Ref. |
| NaOCl | *m*CPBA |
| **2.22** | yield 76%  ee 54% | [72] | **2.23** | conv >99%  ee 46% | [73] |

**Figure 2.6.** Examples of direct linkage to the heterogenized support through the aromatic ring of the Schiff base ligand.

Although, many Mn(salen)-type catalysts have been heterogenised through a heteroatom incorporated into the aromatic ring of the salicylaldehyde, direct anchoring to the aromatic ring of the ligand or immobilization of catalysts through quaternary bonds has also been applied.

The chiral catalyst **2.22** [[72](#_ENREF_72)] (Fig. 2.6) prepared in a process including sol-gel hydrolysis and polycondensation with Si(OEt)4 was employed in the epoxidation of styrenes and isopropylcinnamate (using NaOCl), and the catalyst **2.22** showed higher enantioselectivities but lower yields of epoxides compared to its homogeneous analogue. In the case of complex **2.23** supported by covalent bond on imidazole functionalized mesoporous materials such as SBA-15 [[73](#_ENREF_73)], MCM-41 [[73](#_ENREF_73), [74](#_ENREF_74)], MCM-48 [[73](#_ENREF_73)] and amorphous SiO2 [[73](#_ENREF_73)] (Fig. 2.6), the heterogeneous catalysts exhibited comparable catalytic activity and enantioselectivity to their homogeneous counterpart. The catalyst grafted onto SBA-15 showed the best results, whereas MCM-41-based systems gave the lowest performance in the asymmetric epoxidation of a range of substrates using *m*-CPBA/NMO.

### Manganese Complexes with Schiff-Base Ligands Immobilized on Silica-Based Supports via Complexation of the Manganese Centre

Another well-known type of immobilization strategy is based on linking an embedded axial ligand with the manganese centre of the catalyst. The consequences of this ligation of Mn(salen) to the different supported ligands have been intensively explored and several Jacobsen’s type supported compounds have been synthesized and are depicted as they have been reported in Figures 2.7 and 2.8. However, in some articles, the structures were reported as the primary amine being deprotonated, which seems unlikely given their acidity and the reaction conditions used and we have therefore presented them as primary amine donors.



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | | matrix | Ref. |
| *m*CPBA | NaOCl | TBHP |
| **2.24** | conv 40%, select 90%, ee 38% | - | - | Silica (FSM-16) | [75] |
| **2.25** | conv 22%, select 64%, ee 14% | - | - | Silica (FSM-16) | [77] |
| **2.26** | conv 91%, ee 42% | - | - | MCM-41-type | [79] |
| **2.27** | conv 96%, ee 46% | - | - | MCM-41-type | [80] |
| **2.28** | - | - | conv 73%, select 70% | Silica gel | [81] |
| **2.29** | - | conv 81%, ee 85% | - | Polysiloxane and silica gel | [82] |

**Figure 2.7**. Examples of reported heterogenised complexes through axial ligation.

The Jacobsen’s catalyst derivatives **2.24**-**2.25** (Fig. 2.7) applied in the asymmetric epoxidation of alkenes, were linked through an axial coordination bond with the manganese centre to silica MCM-41 [[75](#_ENREF_75), [76](#_ENREF_76)], Laponite clay [[75](#_ENREF_75), [76](#_ENREF_76)], mesostructured cellular foam (**2.24**/MCF) [[78](#_ENREF_78)], long-axis SBA-15 (**2.24**/lSBA), and short-axis SBA-15 (**2.24**/sSBA) by 3-aminopropyltriethoxysilane (APTES), whereas silica FSM-16 [[75](#_ENREF_75), [77](#_ENREF_77)] was modified by both, APTES or 4-triethoxysilylaniline (TESA) spacer [[77](#_ENREF_77)]. Considering the type of surface, the highest results in styrene epoxidation were obtained using Laponite clays and FSM-16 as the supports. Comparing results for catalysts supported on FSM-16 with APTES and TESA spacers, it was found that in the presence of an APTES spacer, the products were obtained with higher enantiomeric excesses than in the presence of the TESA spacer, although, conversions and epoxide selectivities were comparable in both cases [[77](#_ENREF_77)]. Unfortunately, the catalysts were not stable during recycling, and after a second run ee values often decreased dramatically. The catalysts immobilized on mesostructured cellular foam (**2.24**/MCF) [[78](#_ENREF_78)], long-axis SBA-15 (**2.24**/lSBA), and short-axis SBA-15 (**2.24**/sSBA) were tested in asymmetric epoxidation of *cis*- or *trans*-β-methylstyrene (NaOCl) only.

The ethoxy substituted chiral manganese(III) salen complex **2.26** (Fig. 2.7) was grafted onto APTES modified MCM-41-type mesoporous silica with different amounts of surface amine groups and nanopore sizes. The highest conversion and ee in the epoxidation of indene were obtained for catalysts immobilized on materials in which the alkyl chain length of the template was C18 and the molar ratio of APTES to total Si was 5 [[79](#_ENREF_79)]. The analogous salen catalyst embedded onto MCM-41-type materials via an imidazole linker (**2.27**) [[80](#_ENREF_80)] was prepared using two different methods: co-condensation and grafting. The catalyst **2.27** synthezised in a co-condensation procedure gave better results in styrene oxidation than complex **2.27** obtaind by the grafting method. The catalysts mentioned above were tested in styrene oxidation reactions using *m*CPBA, however, there are some examples of the use TBHP and NaOCl as the terminal oxidant. For instance, the mono-methoxy functionalised manganese salen complex supported on functionalized silica gel **2.28** (Fig. 2.7) [[81](#_ENREF_81)] was used in the catalytic oxidation of styrene with TBHP and gave substrate conversion of 73% with good selectivity for styrene oxide 70%. Whereas, the chiral sulfonato-substituted salen complex **2.29** (Fig. 2.7) immobilized by ion exchange interaction on a polysiloxane and axially coordinated by 3-aminopropyl functionalized silica gel was applied in alkene epoxidation using NaOCl and ionic liquid BMImBF4. Using this reaction system resulted in better performance than with Jacobsen’s catalyst or sulfonato modified Jacobsen’s catalyst in solution [[82](#_ENREF_82)].

In general, the aforementioned catalysts could be reused over several catalytic cycles, however, some of them e.g. **2.27** were characterized by significant decreases in activity during recyclability even in only the second or third cycle.



|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | Matrix | Ref. |
| NaOCl |
| **2.31** | conv 100%, select 100%, ee 59% | Activated silica (pore size 9.7 nm), -C3H6NH-linker | [85] |
| **2.35** | yield 31.2%, ee 39.7% | Activated silica (pore size 9.7 nm) | [88] |

**Figure 2.8**. Catalysts immobilized through axial O-ligation.

Chiral manganese salen catalysts **2.30**-**2.36** have also been axially grafted onto siliceous MCM-41 [[83-85](#_ENREF_83)], SBA-15 [[84](#_ENREF_84), [85](#_ENREF_85)], activated silica [[84](#_ENREF_84), [85](#_ENREF_85)], as well as onto insoluble polystyrene resins [[86](#_ENREF_86)], via organic sulfonic groups without and with different linkage lengths (-CH2-, -CH2-CH2-, -CH2-CH2-CH2-NH-) or phenoxyl groups. Styrene, -methylstyrene, -methylstyrene, 1,2-dihydronaphthalene, 6-cyano-2,2-dimethylchromene and 1-phenylcyclohexene were oxidized using NaOCl/PPNO. In styrene epoxidation the best results of 100% conversion, 96% selectivity and 59% ee were obtained for styrene using **2.31** with a C3H6NH linker supported on activated silica. In the case of 1,2-dihydronaphthalene, epoxidation using **2.32** with a -CH2-CH2-CH2-NH- spacer supported on activated silica gave poorer results with conversions up to 74% and 74% ee. Whereas, oxidation of 1-phenylcyclohexene in the presence of **2.31** supported on the same silica resulted in 100% conversion with 94% selectivity and 65% ee [[85](#_ENREF_85)]. Several manganese catalysts **2.31-2.33** supported on mesoporous materials without a spacer via phenyl sulfonic groups were also applied in -methylstyrene oxidation [[84](#_ENREF_84)]. In these cases, oxidation with the homogeneous catalyst analogues gave better yields (98-100%) than the immobilized complexes (50-87%). In contrast, lower ees were observed for the homogeneous catalysts (26-55%) than for the heterogeneous catalysts (66-78%). Comparing the same complex, **2.32**, immobilized on different supports the most effective system was when then the catalyst immobilized on MCM-41, although the pore size proved to be important and yields and enantioselectivities were higher for the support with pore size 1.6 nm than they were for MCM-41 with pore size 2.7 nm. Oxidation of -methylstyrene under the same reaction conditions was also investigated using **2.31-2.33** and gavethe *cis*-epoxides with good selectivities (*cis*/*trans* ratio in the range 7.71-17.6) and high enantiopurities (92.6-94.8%); this contrasted with the *trans*-epoxide, which dominated under homogeneous conditions [[84](#_ENREF_84)]. The catalysts: **2.32** [[87](#_ENREF_87)] and **2.34-2.36** [[88](#_ENREF_88)] were also used in the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene. The reaction proceeded with the ee of the epoxide product of 90.6% in the presence of the catalyst **2.32** immobilized on activated silica via an alkyl amine spacer, which was somewhat higher than for complex **2.35** supported via phenoxy groups (ee in the range 26.4-84.9%).

Another interesting example, which involved the Mukaiyama-type oxidation of (*R*)-limonene with molecular oxygen, in the presence of isobutyraldehyde and *N*-methyl imidazole was catalyzed by **2.30** (Fig. 2.8) anchored onto sulfonic acid-functionalized SBA-15 molecular sieves [[89](#_ENREF_89)]. It was noted that the *endo*-diastereomer was obtained with an average diastereomeric excess of 40% and that the catalyst was more active than when the manganese complexes were directly supported on SBA-15 or zeolite-Y.



|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | Matrix | Ref. | **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| PhIO | *m*CPBA | PhIO |
| **2.37** | conv 77%, ee 10% | Silica | [90] | **2.40** | - | conv 99%, ee 84% | Silica (NH3+) | [90] |
| **2.38** | conv 34%, ee 82% | **2.41** | conv 96%, ee 67% | conv 41%, ee 88% |
| **2.39** | conv 39%, ee 33% | **2.42** | - | conv 65%, ee 36% |

**Figure 2.9**. Manganese(III) salen catalysts immobilized via multiple interactions.

Also of note are two series of mesoporous helical silica-supported manganese(III) catalysts that were immobilized by different strategies. The complexes **2.37**-**2.39** weretriply immobilized via a mixture of covalent bonding via the salen phenyl rings and axial coordination to the manganese centre, whereas **2.40**-**2.42** were supported by electrostatic interactions between silica and charged substituents on the aromatic rings of the salen ligand. The highest ee of styrene oxide (Fig 2.9) was obtained for **2.41** using PhIO. In contrast the best results in the epoxidation of -methylstyrene (99% ee) and indene (96% ee) were obtained for catalyst **2.41** with *m*-CPBA [[90](#_ENREF_90)]. The combination of the left-handed channels of helical silica with (*R*,*R*)-complex (i.e. **2.38**, **2.41**) was also shown to give higher enantioselectivities than with the (*S*,*S*)-salen analogues (i.e. **2.39**, **2.42**).

### Manganese Complexes with Schiff-Base Ligands Immobilized on Silica-Based Supports via Noncovalent Interactions

Sulfonato modified Jacobsen’s catalyst, analogous to **2.41** (Fig. 2.9, Table 2.1), was also immobilized on silica gel and siliceous earth [[91](#_ENREF_91)], whereas complex **2.41** with Mn(acac)3 was anchored onto silica, resin and LDH materials [[92](#_ENREF_92)]. The epoxidation of styrene was highly enantioselelctive (87% ee) with NaOCl as the terminal oxidant, BMImPF6 as solvent using catalyst **2.41**(Cl) grafted on silica gel (100-200 mesh) [[91](#_ENREF_91)]; these reactions were highly efficient with yields reaching 100% and moderate to excellent enantioselectivities observed under all conditions. Interestingly the catalyst **2.41**(acac) [[92](#_ENREF_92)] supported on LDH and resin showed a slight decrease in enantioselectivity over five catalytic cycles, whereas when embedded on silica a significant erosion of ee was observed.

An interesting development in the field has been the employment of manganese-exchanged Al-MCM-41 modified by the (*R*, *R*)-Jacobsen’s salen ligand (**2.1**, Fig. 2.1) [[93](#_ENREF_93), [94](#_ENREF_94)], (*R*, *R*)-, (*S*, *S*)-Jacobsen’s catalyst (**2.1**, Fig. 2.1) and its achiral analogue (**2.43**, Fig. 2.10) [346]. The solid support was found to be a critical element in the (*Z*)-stilbene oxidation catalyst system and the immobilized complex gave higher *cis*: *trans* ratios of the epoxide products when compared to the non-immobilized complex under the same conditions [[94](#_ENREF_94)]. Unfortunately, the catalyst could not be reused, with conversion decreasing from 78% in the first cycle run to only 18% in the second [[93](#_ENREF_93)].



**Figure 2.10**. An achiral analogue of Jacobsen’s catalyst.

In the oxidation of (*R*)- and (*S*)-limonene, using Oxone® in acetone, higher substrate conversion was obtained in the presence of **2.43**/MCM than non-supported **2.43**. Although, in the oxidation of (*R*)-limonene using the (*R*, *R*)-**2.1**/MCM a higher conversion was reached than in the presence of (*S*, *S*)-**2.1**/MCM, in the reaction of (*S*)-limonene, both supported chiral catalysts gave similar results. However, oxidation of (*R*)-limonene was also shown to occur in the presence of the inorganic catalyst Mn-Al-MCM-41 without any salen ligand present with conversions of 74% and 70% selectivity [346].

Various methods of immobilization have been investigated to support Jacobsen’s catalyst on mesostructured SBA-15 materials, with both pure silica and aluminosilicate (Al/Si = 30) compositions. These catalysts showed good catalytic activities in the enantioselective epoxidation of styrene using *m*-CPBA/NMO; the highest ee of 60% was obtained for a catalyst immobilized by impregnation on SBA-15 by direct ion-exchange on Al/SBA-15, and the best conversion of 73%, which is 18% more than achieved in solution, was achieved using an aminopropyltrimethoxysilane-functionalized SBA-15 [[95](#_ENREF_95)].



**Figure 2.11**. Manganese(III) salen catalysts immobilized via a supported ionic liquid.

Jacobsen’s catalyst and its phenyl analogue were embedded on a [bmim][PF6] (bmin = 1-butyl-3-methylimidazolium hexafluorophosphate) modified ionic liquid supported on MCM-48 (**2.44**, **2.45**) These catalysts were the most effective in the asymmetric epoxidation of -methylstyrene for which conversion and ee could exceed 99%, whereas for the non-immobilized catalyst ee only reached 50%. Oxidation of other alkenes resulted in poorer conversions and ees [[96](#_ENREF_96)].



**Figure 2.12**. Structures of catalysts incorporated into mesoporous nanocages.

Other salen complexes **2.46**-**2.48** (Fig. 2.12) were immobilized by the encapsulation into nanocages of a 3D periodic mesoporous organosilica (PMO). In general, the immobilized dimeric catalysts were shown to give better results in alkene oxidation (NaOCl/4-PPNO) compared to supported monomeric-catalysts and their non-immobilized counterparts, and the best yield of styrene oxide (64%) was obtained using **2.46**/PMO prepared in the absence of NaOH [[97](#_ENREF_97), [98](#_ENREF_98)]. An encapsulation process was also applied to prepare heterogeneous manganese(III)-salophen complex **2.49** by simple diffusion of the salen ligand into a manganese(II) modified diatomite (SiO2·nH2O; a siliceous sedimentary rock) surface. The reactions of epoxidation of aliphatic and aromatic olefins in the presence of the catalyst **2.49** and sodium periodate were characterized by moderate to high conversions, moderate to high yields (99% for cyclooctene), and all of them showed higher activity than the non-immobized counterpart. Moreover, analogous results were obtained in alkane hydroxylation [[99](#_ENREF_99)].

**Table 2.1.** Summarised results of the use of manganese complexes with Schiff-base ligands immobilized on silica-based supports via noncovalent interactions in styrene epoxidation

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| *m*CPBA | NaOCl (or NaIO4) |
| **2.41** | - | yield 100%, ee 87% | silica gel(OH) | [91] |
| **2.41** | yield 100%, ee 44% | - | LDH | [92] |
| **2.1** | yield 73%, ee 49% | - | SBA-15(APR) | [95] |
| **2.44** | conv 50%, ee 41% | - | ionic liquid/MCM-48 | [96] |
| **2.45** | conv 52%, ee 48% | - | ionic liquid/MCM-48 | [96] |
| **2.46** | - | yield 63.6% | organosilica (PMO) | [97] |
| **2.47** | - | yield 57.3% | PMO | [97] |
| **2.48** | - | yield 36.3% | PMO | [97] |
| **2.49** | - | yield 87% (NaIO4) | diatomite | [99] |

### Manganese Complexes with Schiff-Base Ligands Immobilized on other Inorganic Surfaces

#### Manganese Complexes with Schiff-Base Ligands Immobilized on Carbon Materials

|  |  |  |
| --- | --- | --- |
| **Catalyst** | Styrene oxide  (the best conv/yield) | Ref. |
| NaIO4 |
| **2.52** (X = 1,4-diaminobenzene) | Yield 85% | [102] |
| **2.53** (X = 4-aminophenol) | Yield 86% |
| **2.54** (X = 4-aminothiophenol) | Yield 80% |





**Figure 2.13**. Manganese(III) Schiff base complexes immobilized on MWCNTs.

Carbon nanotubes, particulary multi-wall carbon nanotubes (MWCNTs) are another stable material with interesting properties, which have been chosen to anchor organic compounds. For example, the functionalized manganese complexes were covalently grafted onto MWCNTs (**2.50**, **2.51** Fig. 2.13) and their catalytic efficiency was studied in the oxidation of cyclohexene and *para*-xylene. The catalyst **2.50**, tested in cyclohexene oxidation, turned out to be more selective towards 2-cyclohexene-1-one than its homogeneous analogue [[100](#_ENREF_100)]. Whereas, complex **2.51** evaluated in the aerobic oxidation of *para*-xylene resulted substrate conversion in range 30-71% and poor selectivity [[101](#_ENREF_101)].

The analogous manganese(III) salophen complex was supported on differently functionalized MWCNTs using the axial ligand strategy and the resulting heterogeneous catalysts **2.52**-**2.54** [[102](#_ENREF_102)] were employed for epoxidation of cyclic and linear olefins with NaIO4 as the most efficient oxidant. The heterogeneous complex **2.53**, grafted via an aminophenol linker, generally proved to have the highest activity, but all of them yielded the corresponding epoxides with conversions and yields in the range 44-100%. These catalysts were also reused in five consecutive catalytic runs with successive decrease of epoxide yield and a small to moderate leaching of manganese [[102](#_ENREF_102)].



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| *m*CPBA | PhIO |
| **2.55** | - | conv 60% or 31%  select 90% or 68% | Norit® (carbon) | [103] |
| **2.56** | - | conv 13% or 20%  select 84% or 74% | Norit® (carbon) | [103] |
| **2.57** | - | conv 36% or 12%  select 89% or 0% | Norit® (carbon) | [103] |
| **2.59** | conv 48%, ee 5% | - | Activated Carbon(ONa) | [105] |
| **2.60** | conv 59%, ee 31% | - | Activated Carbon(ONa) | [105] |
| **2.60** | conv 74%, ee 43% | - | Activated Carbon(300\_ONa) | [107] |
| **2.60** | conv 24%, ee 41% | - | Carbon xelogel(01CX-09) | [109] |
| **2.61** | - | conv 42%, select 89% | Activated carbon | [110] |
| **2.62** | - | conv 47%, select 83% | Activated carbon(O2 ox) | [110] |
| **2.64** | - | conv 38%, select 81% | Activated carbon(O2 ox) | [112] |
| **2.65** | - | conv 37%, select 74% | Activated carbon(O2 ox) | [111] |

**Figure 2.14**. Carbon supported manganese(III) salen complexes.

In an effort to synthesise different chiral catalysts, manganese(III) salen complexes (L = Cl, OAc) **2.55**-**2.57** (Fig. 2.14), were covalently immobilized on the brominated surface of Norit® (activated carbon) using conventional and microwave heating (MW) conditions [[103](#_ENREF_103)]. The anchored catalyst obtained using the MW heating exhibited greater epoxide selectivitiy in styrene oxidation with iodosylbenzene than both heterogeneous complexes prepared under conventional conditions and its homogeneous counterpart. A hydroxy functionalized Jacobsen-type catalyst was attached onto an amine modified activated carbon through cyanuric chloride with or without an alkyl spacer [[104](#_ENREF_104)], **2.58**, and these catalysts were applied in the epoxidation of -methylstyrene, using NaOCl with modest substrate conversion and ee.

Another pair of manganese hydroxyl-modified Schiff-base complexes were supported by axial coordination of the manganese onto the phenolate groups of functionalized air oxidized carbon (NORIT ROX 0.8, **2.59**, **2.60**, Fig. 2.14) [[105](#_ENREF_105), [106](#_ENREF_106)] and explored in the epoxidation of styrene using PhIO [[106](#_ENREF_106)] or *m*-CPBA/NMO [[105](#_ENREF_105)] and -methylstyrene using NaOCl [[105](#_ENREF_105)]. In general, oxidation reactions carried out in the presence of non-anchored catalysts yielded higher conversions and enantiomeric excesses than with their supported analogues. However, reuse of the heterogeneous catalyst led to no loss of catalytic efficiency with hypochlorite as the oxidant [[105](#_ENREF_105)]. Catalyst **2.60** immobilzed on pore tuned activated carbons with different average pore sizes was also used in the oxidation of 6-cyano-2,2-dimethylchromene and styrene [[107](#_ENREF_107)]. It was observed that selectivity for epoxide formation, enantioselectivity as well as substrate conversion were strongly dependent on pore volume and generally increased with the pore size. Mn(salen)Cl complexes were also immobilized on mesoporous carbon xerogels [[108](#_ENREF_108)], however this did not improve the overall efficiency [[109](#_ENREF_109)]. Manganese complexes **2.61**-**2.65** adsorbed onto an activated carbon and its oxidized forms [[110](#_ENREF_110), [111](#_ENREF_111)] were also tested in PhIO oxidation reactions of styrene. The catalysts **2.61** [[110](#_ENREF_110), [112](#_ENREF_112)], **2.62** [[110](#_ENREF_110)], and **2.64** [[112](#_ENREF_112)] and **2.65** [[111](#_ENREF_111)] (Fig. 2.14) provided a mixture of products with selectivity for styrene oxide in the range 56-89%. However, the bare carbon also exhibited catalytic activity. Heterogeneous catalysts were typically reused without significant loss of selectivity after three cycles, but complex **2.65** was shown to be effective after ten consecutive cycles.



|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | Styrene oxide  (the best conv/yield) | Matrix | Ref. |
| NaOCl |
| **2.66** | conv 99%, ee 40% | graphene | 113 |
| **2.12** | conv 76%, ee 36% | graphene |

**Fig. 2.15**. Graphene oxide functionalised with a Jacobsen-like catalyst.

Jacobsen-type chiral manganese complexes were also anchored onto a functionalized graphene oxide support via imidazolium-based ionic liquid (**2.66**, Fig. 2.15) and amine linkers (**2.12**/graphene, Fig. 2.3). In the alkene oxidation reactions (NaOCl), the ionic liquid functionalized complex **2.66** was the more effective catalyst and gave higher conversions (by between 15-38%) of substrates than **2.12**/graphene. The enantiomeric excesses of epoxides obtained using catalyst **2.66** reached up to93%, however, for some substrates such as styrene, enantioselectivity was rather poor. The catalyst **2.66** did not lose its catalytic activity and enantioselectivity upon reuse and was stable over seven reaction runs [[113](#_ENREF_113)].



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| NaOCl | H2O2 |
| **2.67** | conv >99%, select 97%, ee 49% | - | PWTC | [114] |
| **2.68** | conv >99%, select 96%, ee 29% | - | PWTC | [114] |
| **2.69** | - | yield 58% | Activated carbon(HNO3 ox) | [115] |

**Fig. 2.16**. Complexes supported on pyrolytic waste.

Pyrolytic waste tyre char (PWTC or PC) was also tested as a surface for covalent immobilization of two chiral manganese(III) Jacobsen-type complexes **2.67**, **2.68** [[114](#_ENREF_114)] and imidazole modified imine **2.69** [[115](#_ENREF_115)]depicted in Fig. 2.16. The use of supported catalysts **2.67** and **2.68** in the asymmetric epoxidation of olefins in the presence of NaOCl/PPNO resulted in high conversion (>99%) and selectivities (50-99%) but moderate enantiomeric excesses (29-68%). The catalyst **2.67** maintained its activity in three consecutive reaction cycles, with conversion dropping from 72% in 3rd run to 17% in 4th cycle [[114](#_ENREF_114)]. Catalyst **2.69** [[115](#_ENREF_115)] supported on pyrolitic carbon (PC) and commercial activated carbon (AC) showed also high epoxide selectivities in the oxidation of selected cyclic aliphatic alkenes and styrenes, however, catalyst **2.69-PC** was kinetically faster than **2.69-AC** (1.5 h vs. 5 h).

#### Manganese Complexes with Schiff-Base Ligands Immobilized on Clays and Other Inorganic Supports

The use of inorganic supports including types of clays, carbons and silica gives a variety of possibilities for immobilization, e.g. through covalent bonding and non-covalent interactions. It is difficult to disscuss several types of immobilization for the same ligands separately on the same or similar supports, therefore, in this section there is no classification of the types of embedding.

The same salen complex, which was attached onto graphene and silica (**2.12**, Fig. 2.3, 2.15) was covalently anchored onto APTES modified ceramic ultrafiltration membranes and, after building into a membrane reactor, it was used in the asymmetric epoxidation of styrene. The concentration of APTES influenced catalyst efficiency and the best result, similar to the reaction with the homogeneous salen-Mn(III) catalyst, was obtained when 21 g/L of APTES was applied [[116](#_ENREF_116)]. A different approach was taken to immobilize metal salen complexes via the imine nitrogen atoms.



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | | Matrix | Ref. |
| *m*CPBA | TBHP | PhIO |
| **2.12** | conv 32%, ee 40% | - | - | ceramic membrane reactor | [116] |
| **2.70** | - | conv 51%, select 27% | - | APTES-alumina | [119] |
| **2.77** | - | - | yield 90% | montromorillonite K10 | [120] |

**Figure 2.17**. Linkage of manganese complexes via ‘imine’ nitrogen atoms.

3-Aminopropyltriethoxysilane or 2-aminoethyl-3-aminopropyltrimethoxysilane modified SiO2–Al2O3 mixed-oxide were used as supports for manganese catalysts **2.70**-**2.76** (Fig. 2.17). The catalytic activities of the heterogenized catalysts were studied in the oxidation of ethylbenzene (TBHP) under solvent free conditions [[117](#_ENREF_117)] and in supercritical carbon dioxide [[118](#_ENREF_118)]. The oxidations under solvent free conditions resulted in lower conversions than in *sc*CO2, but catalyst **2.76** showed the highest activity and selectivity, towards acetophenone, in both cases. Structurally similar catalyst **2.70** (L = OAc), prepared by reaction of APTES modified mesoporous alumina with a Schiff-base Mn(III) complex, was utilized in the TBHP oxidation of styrene and cyclohexene leading to the formation of corresponding epoxides with moderate conversion and epoxide selectivity. Hovewer, in this case, the immobilized catalyst proved to be more effective than the corresponding non-immobilized catalyst [[119](#_ENREF_119)]. Apart from SiO2–Al2O3 supports, achiral manganese catalyst **2.77** (Fig. 2.17) was immobilized by a cationic exchange process and by covalent bonding on montromorillonite K10 and silica MCM-41, respectively [[120](#_ENREF_120)]. The catalyst, supported on K10 by a cationic exchange process, yielded higher results in the epoxidation of alkanes using PhIO as terminal oxidant.



**Figure 2.18**. Examples of Mn(III) complexes axially attached to inorganic supports.

Jacobsen’s catalyst was also attached to delaminated zeolites (ITQ-2 and ITQ-6) and silica (MCM-41) by axial ligation (**2.78**, **2.79**) [[121](#_ENREF_121)], whereas salophen manganese(III) catalysts were supported on zeolite Y through axial ligation with the heteropoly acid (HPA) linker (**2.80**) and by a ship-in-a-bottle approach (MnSalophen/Z) [[122](#_ENREF_122)]. The catalytic activity of **2.78**, **2.79** were explored in the epoxidation of selected alkenes using NaOCl as the oxidant. The catalysts axially grafted on zeolites showed similar substrate conversions and enantioselectivities to those embedded on silica, but the axial embedded catalysts on MCM-41 proved to be more enantioselective than the Jacobsen-type catalyst covalently bonded to silica (86% vs 8% ee) [[121](#_ENREF_121)]. Catalyst **2.80** was tested in the oxidation of cyclohexene with isobutyraldehyde as a sacrificial reductant and molecular dioxygen as oxidant and this resulted in higher substrate conversion than MnSalophen/Z and [Mn(salen)Cl]. However, (MnSalophen/Z) gave slightly better epoxide selectivity (92%) than **2.80** (86%) [[122](#_ENREF_122)]. Manganese(III) Schiff base-type complex were also incorporated into zeolite X and Y using the flexible ligand method and tested in the epoxidation of styrene using TBHP as oxidant [[123](#_ENREF_123)].



**Figure 2.19**. Examples of clay-supported manganese(III) Schiff base complexes.

A series of manganese(III) salen complexes depicted on Fig. 2.19 were embedded onto K10-montmorillonite clays (K10) [[124](#_ENREF_124)], aluminium-pillared clays (Alc) [[125-128](#_ENREF_125)], functionalized porous clay heterostructures (PCH) [[129](#_ENREF_129), [130](#_ENREF_130)], organo clays (BEN) [[129](#_ENREF_129)], and laponite clays (Lap) [[75](#_ENREF_75), [76](#_ENREF_76), [131](#_ENREF_131)]. Complex **2.81** was anchored on laponite and aluminium-pillared clays through covalent bonding through cyanuric chloride both with (**2.82**/Lap, **2.82**/Alc) and without (**2.83**/Lap, **2.83**/Alc) an APTES spacer as well as non-covalent interactions (**2.81**/Lap, **2.81**/Alc) [[125](#_ENREF_125), [131](#_ENREF_131)]. Chiral Jacobsen-type catalysts were immobilized via covalent bonding between modified salen complex and modified clays (**2.84**/PCH, **2.84**/BEN, **2.85**/PCH) [[129](#_ENREF_129), [130](#_ENREF_130)] and via coordinative bond of the manganese centre with a phenol group of the modified clay (**2.86**/PCH) [[129](#_ENREF_129)]. Chiral cationic manganese complex (**2.87**) [[124](#_ENREF_124)] was grafted onto montmorillonite clay by cation exchange, whereas complexes **2.88** [[128](#_ENREF_128)], **2.89** [[127](#_ENREF_127)], **2.90** [[127](#_ENREF_127)], **2.91** [[126](#_ENREF_126)], were encapsulated onto different types of aluminium-pillared clays.

The prepared heterogeneous catalysts were examined in the asymmetric epoxidation of olefins using *m*-CPBA, PhIO or NaOCl as the oxygen source. Moreover, all of these solid catalysts could be recycled and used at least two times with only a moderate decrease in their catalytic activity.

**Table 2.2**. The use of immobilized catalysts **2.81**-**2.91** in styrene epoxidation reactions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| *m*CPBA | PhIO (or NaOCl) |
| **2.81**/Lap | - | conv 66%, select 81% | laponite clays | [[131](#_ENREF_131)] |
| **2.83**/Lap | - | conv 42%, select 65% |
| **2.82**/Lap | - | conv 35%, select 61% |
| **2.81**/Alc | - | Conv 35%, select 80% | aluminium-pillared clays | [[125](#_ENREF_125)] |
| **2.83**/Alc | - | conv 38%, select 29% |
| **2.82**/Alc | - | conv 46%, select 18% |
| **2.84**/BEN | conv 14%, select 71%, ee 5% | - | organo clays | [[130](#_ENREF_130)] |
| **2.84**/PCH | conv 33%, select 84%, ee 6% | - | porous clay heterostructures | [[130](#_ENREF_130)] |
| **2.85** | conv 45%, select 87%, ee 18% | - | [[129](#_ENREF_129)] |
| **2.86** | conv 40%, select 79%, ee 7% | - | [[129](#_ENREF_129)] |
| **2.87** | conv 99%, select 93%, ee 6% | - | montmorillonite | [[124](#_ENREF_124)] |
| **2.88** | - | conv 43%, select 75% | aluminium-pillared clays | [[128](#_ENREF_128)] |
| **2.89** | conv 15-19%, ee 1-4% | conv 18-40%, ee 1-14% | [[127](#_ENREF_127)] |
| **2.90** | conv 19%, ee 0% | conv 32%, ee 2% | [[127](#_ENREF_127)] |
| **2.91** | - | conv 35-64%, select 59-62% (NaOCl) | [[126](#_ENREF_126)] |

In styrene oxidation all the catalysts used demonstrated low activity, and the best ee of 54% was obtained in the presence of **2.81**/Lap. In terms of conversion and yield of epoxide product, compounds immobilized on K10 by an ion-exchange approach facilitated the highest results. Some differences between immobilization method and support have also been observed, for example, **2.81** immobilized by covalent and non-covalent bonding on laponite showed significantly higher yield than on aluminium pillared clays. Another type of “clay” used to immobilize catalysts was modified bentonite. In this approach mixed Co-Mn nanoparticles functionalized with salen ligands were immobilized on the clay and tested in the oxidation of *p*-xylene [[132](#_ENREF_132)].



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| NaOCl | other |
| **2.92** | - | yield 79% (NaIO4) | montmorillonite | [133] |
| **2.93** | yield >99%, ee 45% | - | [134] |
| **2.94** | yield 99%, ee 44% | - |
| **2.95** | yield >99%, ee 52% | - |
| **2.96** | yield >99%, ee 41% | - |
| **2.97**  (Scheme 2.21) | - | conv 71%, select 88%, ee 18% (O2/pivaldehyde) | LDH | [136] |

**Figure 2.20**. Montmorillonite clay supported catalysts.

In an analogous manner, the cationic Mn(III) complexes **2.92** [[133](#_ENREF_133)] and **2.93**-**2.96** [[134](#_ENREF_134)] were also exchanged in montmorillonite clay. The immobilized catalyst **2.92** exhibited good catalytic activity for alkane hydroxylation and linear and cyclic alkenes epoxidation using NaIO4 [[133](#_ENREF_133)], whereas, the complexes **2.93**-**2.96** [[134](#_ENREF_134)] were tested in the enantioselective epoxidation of alkenes in the presence of NaOCl/PyNO, only [[134](#_ENREF_134)].



**Figure 2.21**. Chemoselective epoxidation by supported catalyst **2.97**.

The analogous manganese(III) sulfonato-salen complex as applied in preparation heterogeneous catalyst **2.41** (Fig. 2.9), was intercalated into positively charged Zn/Al layered double-hydroxide (LDH) material (**2.97**) and its catalytic efficacy investigated in the oxidation of a range of substrates, including cyclohexene [[135](#_ENREF_135)], substituted cyclohexenes [[136](#_ENREF_136)], dicyclopentadiene [[135](#_ENREF_135)], 1,5-cyclooctadiene [[137](#_ENREF_137)], styrene and methylstyrenes [[136](#_ENREF_136)], (*R*)-limonene [[138](#_ENREF_138), [139](#_ENREF_139)], and (−)-α-pinene [[139](#_ENREF_139), [140](#_ENREF_140)], in the presence of molecular oxygen at atmospheric pressure, pivaldehyde and *N*-methylimidazole. Epoxidation of selected alkenes e.g. diene **2.98** afforded a mixture of two different mono-epoxides **2.99** and **2.100** respectively (as depicted in Fig. 2.21), while other substrates, e.g. dicyclopentadiene, were only converted into their corresponding mono-epoxides.



**Figure 2.22**. Selection of solid-supported manganese complexes.

Several manganese(II) complexes were immobilized on various inorganic supports, i.e. Mn(II) complexes with magnetic moments µeff in the range 5.86-5.93 B, were supported on acidic alumina (A) [[141-146](#_ENREF_141)] and zeolite Y (Z) [[147-153](#_ENREF_147)] and formed heterogenised catalysts labeled **2.101**/A [[141](#_ENREF_141)], **2.102**/A [[142](#_ENREF_142)], **2.103**/A [[143](#_ENREF_143)], **2.104**/A [[144](#_ENREF_144)], **2.109**/A [[145](#_ENREF_145)] and its non-methylated analogues **2.108**/A [[154](#_ENREF_154)], **2.110**/A [[146](#_ENREF_146)], as well as **2.111**/Z-**2.121**/Z, respectively. Only complexes **2.105**-**2.107** were synthesized as manganese(III) derivatives with their magnetic moments µeff found to be in the range 4.89-4.91 B and were embedded into zeolites [[151](#_ENREF_151)]. The complexes were embedded into zeolite Y using two different techniques i.e. manganese(II) derivatives **2.119**/Z [[152](#_ENREF_152)], **2.117**/Z, **2.118**/Z [[150](#_ENREF_150)], **2.112**/Z-**2.115**/Z [[148](#_ENREF_148)], and manganese(III) **2.105**/Z-**2.107**/Z [[151](#_ENREF_151)] complexes were encapsulated into the nanopores of the zeolite; whereas manganese(II) complexes **2.121**/Z [[153](#_ENREF_153)], **2.116**/Z [[149](#_ENREF_149)], **2.111**/Z [[147](#_ENREF_147)] were entrapped in the nanocavity of the zeolite. Then alumina and zeolite-supported manganese(II) complexes, were tested in cyclohexene oxidation with TBHP and H2O2 and showed good activity (Table 2.3).

**Table 2.3**. The best results obtained in the oxidation of cyclohexene with TBHP or H2O2 catalyzed by manganese(II) complexes **2.101**-**2.121** grafted onto inorganic supports.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | Oxidant | Conversion  [%] | Selectivity [%] | | | | Ref. |
| 2-cyclohexene-1-one | 2-cyclohexene-1-ol | cyclohexanone | cyclohexanol |
| **2.101**/Aa | TBHP | 80.7 | 79.9 | 15.2 | - | - | [[141](#_ENREF_141)] |
| **2.102**/Aa | TBHP | 81.7 | 79.4 | 13.5 | - | - | [[142](#_ENREF_142)] |
| **2.103**/Aa | TBHP | 81.4 | 75.91 | 15.36 | - | - | [[143](#_ENREF_143)] |
| **2.104**/Aa | TBHP | 84.3 | 80.9 | 12.4 | - | - | [[144](#_ENREF_144)] |
| **2.109**/Aa | TBHP | 82.8 | 80.5 | 14.2 | - | - | [[145](#_ENREF_145)] |
| **2.110**/Aa | TBHP | 91.3 | 87.6 | 10.6 | - | - | [[146](#_ENREF_146)] |
| **2.111**/Za | TBHP | 85.1 | 86.3 | 12.8 | - | - | [[147](#_ENREF_147)] |
| **2.112**/Zb | TBHP | 73.9 | 8.3 | 4.6 | - | - | [[148](#_ENREF_148)] |
| **2.113**/Zb | TBHP | 72.1 | 7.3 | 3.5 | - | - | [[148](#_ENREF_148)] |
| **2.114**/Zb | TBHP | 90.5 | 12.4 | 1.3 | - | - | [[148](#_ENREF_148)] |
| **2.115**/Zb | TBHP | 85.2 | 9.4 | 9.0 | - | - | [[148](#_ENREF_148)] |
| **2.116**/Z | TBHP | 92.5 | 90.8 | 9.2 | - | - | [[149](#_ENREF_149)] |
| **2.117**/Z | H2O2 | 6.5 | - | - | 91.3 | 8.7 | [[150](#_ENREF_150)] |
| **2.118**/Z | H2O2 | 15.3 | - | - | 73.2 | 26.8 | [[150](#_ENREF_150)] |
| **2.120**/Z | H2O2 | 8.7 | - | - | 31.6 | 68.4 | [[152](#_ENREF_152)] |
| **2.121**/Z | H2O2 | 8.4 | - | - | 74.1 | 25.9 | [[153](#_ENREF_153)] |

The formation of the following products also occurred: a1-(*tert*-butylperoxy)-2-cyclohexene, b1-(*tert*-butylperoxy)-2-cyclohexene and di(2-cyclohexenyl)ether.

Oxidation of cyclohexene in the presence of heterogenised catalysts and TBHP typically gave major products such as 2-cyclohexene-1-one, 2-cyclohexene-1-ol contaminated with 1-(tert-butylperoxy)-2-cyclohexene and sometimes di(2-cyclohexenyl)ether (see Table 2.3), however reaction with **2.116**/Z resulted in the formation of ketone and alcohol, only. In contrast, oxidation with H2O2 yielded a mixture of cyclohexanone and cyclohexanol with low substrate conversion (up to 15.3%), but quite high alcohol selectivity (68.4%). The reaction performed with alumina and zeolite Y based catalyst with TBHP displayed similar, high conversions (72.1- 92.5%), but much better selectivity was obtained using an alumina supported catalyst (Table 2.3, entry 1-8) than one embedded on zeolite (Table 2.3, entry 9-13). Catalysts supported on zeolite gave much higher conversion with the oxidant TBHP than with H2O2. Manganese(III) catalysts **2.105**/Z-**2.107**/Z were used in the oxidation of styrene and the mixture of products, mainly benzaldehyde and styrene oxide, were obatined with high conversion, but poor epoxide selectivity (up to 37.4%) [[151](#_ENREF_151)]. Most catalysts were recycled to test their stability, after the third and fourth runs a slight decrease of catalyst activity was observed. In addition, **2.103** supported on -zirconium phosphate [[155](#_ENREF_155)] was explored for TBHP oxidation of cyclohexane with moderate conversion (25%) but high Ketone:Alcohol (K:A) selectivity (97%).

Catalyst **2.103** was also immobilized on zirconium dioxide through hydrogen bonds between the manganese(III) salen and the ZrO2 [[156](#_ENREF_156)]. This novel catalyst was utilized in the aerobic oxidation of styrene and showed moderate conversion of styrene (up to 81%) with modest selectivity toward styrene oxide (up to 47%).



**Figure 2.23**. Manganese(III) Schiff base complexes occluded into modified zeolites.

Different transition metal Schiff-base complexes, including manganese(III) illustrated in Fig.2.23 (L = Cl), were also occluded into modified zeolites (X, Y and DAY) via a ship-in-a-bottle strategy and the supported catalysts were tested in the stereoselective oxidation of (*R*)-limonene (complex **2.1**/Z) [[157](#_ENREF_157)] and (-)--pinene (complexes **2.124**/Z-**2.127**/Z) [[158](#_ENREF_158)] using dioxygen and pivalaldehyde. Oxidation of these substrates resulted in high substrate conversions but moderate selectivity and diastereoselectivity. For example, the epoxidation of -pinene using **2.124**/Z and **2.127**/Z gave the highest epoxide selectivites (85-87%), whereas using **2.124**/Z and **2.125**/Z exhibited the highest diastereomeric excesses (92-96%) toward (-)--pinenoxide [[158](#_ENREF_158)]. The ship-in-the-bottle synthesis approach was also applied to occlude Jacobsen’s catalyst in zeolite MCM-22, which was used for the catalytic epoxidation of α-methylstyrene and exhibited higher enantioselectivity than its homogeneous counterpart (91.3% vs 51% ee) [[159](#_ENREF_159)]. In another approach the Keggin-type polyoxometalate (POM) skeletons were used to immobilize chiral manganese(III) salen complexes **2.122**/POM (L = ClO4) [[160](#_ENREF_160)]. The catalytic efficiency of the hybrid material obtained with the formula [Mn(salen)(CH3OH)(H2O)]2[Mn(salen)(CH3OH)](PX12O40)] (X = Mo or W) were studied in the asymmetric epoxidation of chromene derivative using NaOCl/4-PPNO as oxidant, and the reaction afforded good conversions and product ee’s in the range 41-43%.



**Figure 2.24**. Schiff base-containing ligands also supported on zeolites.

To facilitate oxidation of cyclohexene, other hetereogenous catalysts Mn-**2.128**/Z (consisting of a Schiff base ligand **2.128** and Mn(II)-exchanged zeolite Y) and Mn-**2.129**/Z (complex Mn-**2.129** enclosed in the nanopores of a zeolite Y) were applied. The higher conversion of alkene was obtained using Mn-**2.128**/Z and H2O2 as the oxygen source [[161](#_ENREF_161)] rather than Mn-**2.129**/Z and TBHP [[162](#_ENREF_162), [163](#_ENREF_163)].

### Conclusions

A vast range of examples of synthetic applications of silica-based supports e.g. mesoporous silica and mesoporous functionalized silica (including MCM-41, MCM-48, SBA-15, HMS, FSM-16, MCF, PMO and natural diatomite) as well as other carriers such as carbon materials (e.g. carbon nanotubes (MWCNTs), activated carbon, graphite and even pyrolytic waste), zeolites and clays (montmorillonite, laponite clay, organo clays), LDH and POM materials, membranes and membrane reactors have been reported recently in the literature in the field of catalytic oxidation of hydrocarbons. The salen-manganese species could be embedded on these surfaces via i) formation of a new covalent bond (i.e. carbon-carbon, nitrogen-carbon, sulfur-carbon, and oxygen-carbon) between the salen benzene ring or the imine moiety and an anchoring group of the support; ii) via axial coordination between the manganese ion of the salen complex and a functional group of the material, and iii) non-covalent interaction e.g electrostatic interactions between the surface and manganese-salen complex.

The increase of efficiency of immobilized catalysts or formation of oxidation products with opposite chemoselectivity compared to their non-supported counterparts was sometimes observed, but there is no universal relationship between them, and typically yields and enantiomeric excesses obtained in the presence of heterogeneous catalysts were similar or lower than those obtained under analogous homogeneous conditions [[18](#_ENREF_18)]. However, in several examples, much better enantioselectivities were observed in the presence of the heterogeneous catalyst but this was often accompanied by lower conversions or yields. The main adavantages of using catalysts embedded on inorganic supports, which are relatively stable, is their ability to be recycled and reused, typicaly over 3-6 consecutive cycles. However, some of them could only be used once in catalytic oxidations due to the significant loss of catalyst activity caused by degradation of the catalyst and leaching of manganese. The activities of heterogeneous catalysts depend on the method of immobilization and chemical structure of immobilized molecule as well as the properties of the support, including the chemical composition of the support, porosity of surface and even the method of support preparation. There are no clear trends to indicate what type of catalyst immobilization would give better catalytic efficiency and catalyst stability.

## Manganese Complexes with Schiff-Base Ligands Immobilized on Inorganic-Organic Hybrid Supports

### Manganese Complexes with Schiff-Base Ligands Immobilized on Polymeric Phosphates

Organic polymer-inorganic phosphate salt hybrid materials composed of various phosphate salts (Zr, Zn, Al, and Ca [[164](#_ENREF_164)]) with oligostyrenylphosphonate or with co-polymers of styrene and phenylvinylphosphonate or isopropenylphosphonate have found widespread application as catalyst supports in oxidation reactions.

#### Manganese Complexes with Schiff-Base Ligands Immobilized on Polymeric Phosphates via Covalent Bonding

Similar strategies to those described earlier (see section 2.1.1) have been employed to immobilize Jacobsen-type catalysts. Generally, the structures of these solid catalysts can be designed by functionalization of different material matrices with linkers and spacers to achieve different organic-inorganic architectures, which lead to disparate results. Much effort has been devoted to the preparation of zirconium phosphate-phosphonate derivatives Zr-SPP (zirconium oligo-styrenyl phosphonate hydrogen phosphates), Zr-PS-IPPA (zirconium poly(styrene-isopropenyl phosphonate)-phosphate), Zr-PS-PVPA zirconium poly(styrene-phenylvinylphosphonate)-phosphate) and their application as supports in immobilizing chiral manganese(III) salen complexes.



**Figure 2.25**. An analogue of Jacobsen’s catalyst mounted on Zr-SPP.

A chiral Jacobsen-type manganese(III) complex, covalently attached through the phenyl group of the Schiff base ligand onto a class of inorganic–organic hybrid materials— zirconium oligo-styrenyl phosphonate hydrogen phosphates (Zr-SPP) [[165](#_ENREF_165), [166](#_ENREF_166)], was explored in the enantioselective epoxidation of selective olefins. Although, the complex **2.130** provided higher enantioselectivity than Jacobsen’s catalyst in -methylstyrene oxidation [[165](#_ENREF_165)] using PPNO/NaOCl, epoxidation of styrene and indene proved to be more effective using the *m*-CPBA/NMO catalytic system [[166](#_ENREF_166)].

#### Manganese Complexes with Schiff-Base Ligands Immobilized on Polymeric Phosphates via Axial Coordination

Jacobsen’s catalyst has also been axially immobilized onto modified inorganic–organic hybrid materials using a range of different supports and linkers which are summarised in Table 2.4.



**Figure 2.26**. Examples of axially supported analogues of Jacobsen’s catalyst.

Jacobsen’s complex was embedded through axial coordination of a diamine (e.g. alkyl amine with different linkage lengths or aryl amine) on modified Zr-SPP (**2.131**, Fig 2.26) [[167](#_ENREF_167)] and its aluminium analogue Al-SPP (**2.132**)[[168](#_ENREF_168)], but also on zirconium poly(styrene-phenylvinylphosphonate)-phosphate (Zr-PS-PVPA) and zirconium poly(styrene-isopropenyl phosphonate)-phosphate (Zr-PS-IPPA). These catalysts immobilized on Zr-PS-PVPA including **2.133** [[169](#_ENREF_169)], **2.** **134** with polyamine linkers [[169](#_ENREF_169)], **2.138**, **2.139** with aryl diamines linkers [[171-173](#_ENREF_171), [177](#_ENREF_177)], **2.140** possessing a “click” generated 1,2,3-triazole linker [[174](#_ENREF_174), [175](#_ENREF_175)], and **2.141**, **2.142** with an azole onium linker [[176](#_ENREF_176)], showed good chiral induction for the asymmetric epoxidation of selected alkenes under oxidation conditions with NaOCl/PPNO or *m*-CPBA/NMO (Table 2.4). The complexes **2.135** (Fig 2.26), with an alkyl diamine linker, **2.136** and **2.137**, with aryl diamine linkers, were synthesized in the same manner and supported on Zr-PS-IPPA material [[170](#_ENREF_170)]. The most effective complexes embedded on Zr-PS-PVPA were catalysts **2.134**(n = 4), **2.138**, **2.140**, and **2.141** especially for α-methylstyrene, where both the conversion and enantiometric excess of the epoxide could exceed 99% at rt. The complex **2.135** (n = 6) supported on Zr-PS-IPPA [[170](#_ENREF_170)] also gave ee ˃99% in this reaction but the yield only reached 67.9%. Typically, the immobilized catalysts showed better performance than the homogeneous Jacobsen’s catalysts, and were reused with relatively little loss of activity and enantioselectivity after ten catalytic cycles.



**Figure 2.27**. Axially supported catalysts using sulfonate linkers.

Chiral salen complexes have been supported by axial coordination with a variety spacer lengths onto sulfoalkyl-modified Zr-PS-IPPA [[178](#_ENREF_178), [179](#_ENREF_179)], Zr-PS-PVPA [[178](#_ENREF_178)] and Zn-PS-PVPA [[180](#_ENREF_180)] and on functionalized zirconium phosphonates with mesoporous channels and different arm lengths of alkylsulfonic linkage [[181](#_ENREF_181)] (Fig. 2.27). [[178](#_ENREF_178)]. In general, the mesoporous zirconium phosphonates (**2.145**) and Zr-PS-PVPA supported catalysts (**2.143**) were found to be more active than the Zr-PS-IPPA-based catalysts **2.144** (see Table 2.4).



**Figure 2.28**. Axially supported catalysts using phenoxy and alkoxy linkers.

In addition to amine and sulfonic linkers, phenoxy and alkoxy linkers were also applied for the axial immobilization of Jacobsen’s catalyst onto zirconium [[182](#_ENREF_182), [183](#_ENREF_183)] or zinc [[97](#_ENREF_97)] PS-PVPA (Fig. 2.28), as well as onto aluminium oligo-styrenyl phosphonate hydrogen phosphates (Al-SPP) [[185](#_ENREF_185)]. The phenoxy-modified heterogeneous catalysts **2.146**, **2.147**, **2.148** immobilized on Zr-PS-PVPA [[182](#_ENREF_182), [183](#_ENREF_183)] showed better good ee values under *m*-CPBA-based conditions, while, catalysts supported on Zn-PS-PVPA [[97](#_ENREF_97)] were more effective in NaIO4-promoted epoxidations. Synthesized in a similar manner, the catalysts **2.149**, **2.150**, **2.151** when used in the oxidation of styrene, -methylstyrene and indene with *m*-CPBA as oxidant, also proved effective with good conversions and enantioselectivities [[184](#_ENREF_184)]. The Al-SPP surface has also been used to immobilize manganese complexes via alkyl (**2.152**) or glycolyl linker (**2.153**) [[185](#_ENREF_185)]. These catalysts provided a significant increase in conversion and ee values without the need for coordinating axial bases such as NMO e.g. for indene oxide an ee of 94% was reported when only *m*-CPBA was used, which was eroded to 35% by the addition of NMO. The same linear linkers were also used to form manganese(III) caytalysts immobilized on Zr-PS-PVPA [[186](#_ENREF_186)] materials. Catalyst **2.155** with glycolyl linkage showed slightly better enantioselectivity than **2.154**,with an alkyl linker under *m*-CPBA-based conditions.

In general, all the axially ligated analogues of Jaobsen’s catalyst exhibited good to excellent activity in the epoxidation of typical olefins, often with higher values than were gained in analogous homogeneous conditions. Immobilization on these materials also enhanced the stability and reusability of Jacobsen’s catalyst up to thirteen reaction cycles. The best results of representative supported catalysts are summarized in Table 2.4. However, it should be noted that for compounds **2.140** and **2.141** absolutely identical results have been presented in the asymmetric epoxidation of α-methylstyrene in separate publications, which appears inconsistent with the observations of others working in the area.

**Table 2.4**. The best results of alkene epoxidation obtained using selected catalyst supported on inorganic–organic polymer hybrid materials.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Substrate | **Catalyst** | Support | Oxidant | Efficacy | | ee [%] | Ref. |
| yield [%] | conv [%] |
| Styrene | Jacobsen’s catalyst | - | different conditions |  | up to ˃99 | up to 54 | [[167](#_ENREF_167), [169](#_ENREF_169), [170](#_ENREF_170), [174](#_ENREF_174), [175](#_ENREF_175), [178](#_ENREF_178), [182](#_ENREF_182), [184](#_ENREF_184)] |
| **2.131**(n=6) (*5th run*) | Zr-SPP | *m*-CPBA/NMO, -78 °C, 1h | 56 (*44*) |  | 72 (*59*) | [[167](#_ENREF_167)] |
| **2.134**(n=4) | Zr-PS-PVPA | m-CPBA/NMO, -20 °C, 6h |  | 98 | 72 | [[169](#_ENREF_169)] |
| **2.135**(n=6) | Zr-PS-IPPA | m-CPBA/NMO, -10 °C, 1h | 92.8 |  | 45.5 | [[170](#_ENREF_170)] |
| **2.140**(n=6) | Zn-PS-PVPA | *m*-CPBA, 0 °C, 1h | ˃99 |  | 73.5 | [[174](#_ENREF_174), [175](#_ENREF_175)] |
| **2.143**(CH2OCH2CH2) | Zr-PS-PVPA | NaOCl/PPNO, 20 °C, 24h |  | 62 | 59 | [[178](#_ENREF_178)] |
| **2.144**(CH2OCH2CH2) | Zr-PS-IPPA | NaOCl/PPNO, 20 °C, 24h |  | 58 | 48 | [[178](#_ENREF_178)] |
| **2.148** | Zr-SPS-PVPA | *m*-CPBA, 0 °C, 1h |  | 99.9 (select 96%) | 31.6 | [[182](#_ENREF_182)] |
| **2.151** | Al-SPP | *m*-CPBA, 0 °C, 12h |  | 97 | 80 | [[184](#_ENREF_184)] |
| -methylstyrene | Jacobsen’s catalyst | - | different conditions |  | up to ˃99 | up to 54 but 99 (NaIO4/imidazole) | [[168-171](#_ENREF_168), [174-176](#_ENREF_174), [178](#_ENREF_178), [182](#_ENREF_182), [184-186](#_ENREF_184)] |
| **2.132**(n=3) (*10th run*) | Al-SPP | *m*-CPBA, -20 °C, 6h |  | ˃99.9 (*84.5*) | ˃99.9  (*83.1*) | [[168](#_ENREF_168)] |
| **2.134**(n=4) (*13th run*) | Zr-PS-PVPA | NaOCl/PPNO, rt, 24h |  | ˃99 (*58*) | ˃99(*65*) | [[169](#_ENREF_169)] |
| **2.135**(n=6) (*8th run*) | Zr-PS-IPPA | NaOCl/PPNO, 0 °C, 24h | 67.9 (*40.3*) |  | ˃99.5 (*68.5*) | [[170](#_ENREF_170)] |
| **2.140**(n=6) (*12th run*) | Zn-PS-PVPA | *m*-CPBA, -40 °C, 5h |  | ˃99 (*32.7*) | ˃99 (*20*) | [[174](#_ENREF_174), [175](#_ENREF_175)] |
| **2.141** (*12th run*) | Zn-PS-PVPA | *m*-CPBA, -40 °C, 5h  NaIO4, 25 °C, 5h |  | ˃99 (*32.7*) | ˃99 (*20*) | [[176](#_ENREF_176)] |
| **2.138**(X = *p*-NH-C6H4-NH; 0.33) (*12th run*) | Zn-PS-PVPA | *m*-CPBA, -40 °C, 5h  NaIO4, 25 °C, 7h |  | ˃99 (*73*) | ˃99 (*29.4*) | [[171](#_ENREF_171)] |
| **2.143**(CH2OCH2CH2) (*10th run*) | Zr-PS-PVPA | NaOCl/PPNOc |  | 79 (*54*) | 91 (*60*) | [[178](#_ENREF_178)] |
| **2.144**(CH2OCH2CH2) (*10th run*) | Zr-PS-IPPA | NaOCl/PPNO, 20 °C, 24h |  | 70 (*32*) | 84 (*58*) | [[178](#_ENREF_178)] |
| **2.148** (*11th run*) | Zr-SPS-PVPA | *m*-CPBA, 0 °C, 1h (5h) |  | 99.9 (select 60.9% ) (*43.6, select 39.9%)* | 73.7 (*54.4*) | [[182](#_ENREF_182)] |
| **2.151** | Al-SPP | *m*-CPBA, 0 °C, 12h |  | 99 | 99 | [[184](#_ENREF_184)] |
| **2.152**(n=6) | Zr-PS-PVPA | *m*-CPBA, 0 °C, 6h | 81 |  | 95 | [[185](#_ENREF_185)] |
| **2.155** | Zr-PS-PVPA | *m*-CPBA, 0 °C |  | >99, (select 62%) | 82 | [[186](#_ENREF_186)] |
| Indene | Jacobsen’s catalyst | - | different conditions |  | up to 99 | up to 65% | [[168](#_ENREF_168), [170](#_ENREF_170), [171](#_ENREF_171), [174-176](#_ENREF_174), [178](#_ENREF_178), [182](#_ENREF_182), [184-186](#_ENREF_184)] |
| **2.132**(n=4) | Al-SPP | *m*-CPBA, 0 °C, 4h |  | 97.7 | 95.0 | [[168](#_ENREF_168)] |
| **2.135**(n=6) | Zr-PS-IPPA | *m*-CPBA/NMO, -10 °C, 1h | ˃99 |  | ˃99 | [[170](#_ENREF_170)] |
| **2.140**(n=6) | Zn-PS-PVPA | *m*-CPBA, 0 °C, 1h | ˃99 |  | ˃99 | [[174](#_ENREF_174), [175](#_ENREF_175)] |
| **2.141** | Zn-PS-PVPA | *m*-CPBA, 0 °C, 1h | ˃99 |  | ˃99 | [[176](#_ENREF_176)] |
| **2.138**(X = *p*-NH-C6H4-NH; 0.33 | Zn-PS-PVPA | *m*-CPBA, 0 °C, 1h |  | ˃99 | ˃99 | [[171](#_ENREF_171)] |
| **2.143**(CH2OCH2CH2) | Zr-PS-PVPA | NaOCl/PPNO, 20 °C, 24h |  | 88 | ˃99 | [[178](#_ENREF_178)] |
| **2.144**(CH2OCH2CH2) | Zr-PS-IPPA | NaOCl/PPNO, 20 °C, 24h |  | 74 | 98 | [[178](#_ENREF_178)]176 |
| **2.148** | Zr-PS-PVPA | *m*-CPBA, 0 °C, 1h |  | 99.9 | 99.5 | [[182](#_ENREF_182)] |
| **2.151** | Al-SPP | *m*-CPBA, 0 °C, 12h |  | 97 | 98 | [[184](#_ENREF_184)] |
| **2.152**(n=6) | Zr-PS-PVPA | *m*-CPBA, 0 °C, 6h | 94 |  | 97 | [[185](#_ENREF_185)] |
| **2.155** | Zr-PS-PVPA | *m*-CPBA, 0 °C |  | 96 (select 96%) | ˃99 | [[186](#_ENREF_186)] |
| oct-1-ene | Jacobsen’s catalyst | - | NaOCl/PPNO, 20 °C, 6h | 90 |  | 40 | [[178](#_ENREF_178)] |
| **2.143**(CH2OCH2CH2) | Zr-PS-PVPA | NaOCl/PPNO, 20 °C, 24h |  | 95 | 69 | [[178](#_ENREF_178)] |
| **2.144**(CH2OCH2CH2) | Zr-PS-IPPA | NaOCl/PPNO, 20 °C, 24h |  | 95 | 75 | [[178](#_ENREF_178)] |

### Manganese Complexes with Schiff-Base Ligands Immobilized on Coordination Polymers and Metal-Organic Frameworks

In the past two decades, the growth in the synthesis and applications of Coordination Polymers (CPs) and Metal-Organic Frameworks (MOFs) [[187](#_ENREF_187)] in different research fields has been marked. Various terminologies have been used to describe compounds consisting of metal ions or metal-containing clusters linked by coordination bonds to organic ligands to form one, two, or three dimensional structures [[188](#_ENREF_188), [189](#_ENREF_189)]. In terms of recommended IUPAC terminology, CPs are straight-chain compounds (1D) only, whereas 2D and 3D structures are referred to as MOFs, i.e. coordination compounds “with an open framework containing potential voids” and porous coordination polymers (PCPs) [[190](#_ENREF_190)]. There are several examples of the use these materials as the supports in manganese catalysed reactions.



**Figure 2.29**. Manganese complexes incorporated into coordination polymers.

The first example of the application of manganese(III) CPs in asymmetric epoxidation utilized various metal cation centers (Cu, Cr, Cd, Mn, Mg, Co, Zn, Fe, and Ni) that were linked by a bidentate ligand [bis(catechol)salen]MnCl (**2.156**) [[191](#_ENREF_191)]. The Mn-**2.156**-CP yielded 2,2-dimethyl-2H-chromene oxide with the highest yield, but moderate enantioselectivity, but the use of Cu, Cd, Mg, and Zn based CP resulted in a higher ee (76%). Catalyst Cu-**2.156**-CP showed good recyclability, because only a 9% decrease in yield of epoxide was observed after ten catalytic runs, and no decrease of enantioselectivity was observed, despite a simultaneous leaching of manganese and copper during the first two cycles. In simmilar manner, a number of lanthanide-based (Nd, Eu, Gd, Tb, and Dy) 1D CPs containing manganese salen units **2.157** [[192](#_ENREF_192)] were prepared, and then tested in the catalytic epoxidation of *trans*-stilbene with molecular oxygen using synthetic air.



**Figure 2.30**. Complexes incorporated into isoreticular CMOFs.

The catalytic efficiency of a series isoreticular chiral metal-organic frameworks (CMOFs) with different cavity sizes and topology (pcu – primitive cubic lattice or lcy – lattice complex *Y*) obtained from the reaction of zinc nitrate hexahydrate with salen modified dicarboxylate ligands **2.158**-**2.161** (L = Cl, Fig. 2.30) were evaluated for catalytic asymmetric epoxidation of selected olefins including indene, 2,2-dimethyl-2*H*-chromene and 6-substituted (e.g. Me, MeO, NO2, CN) 2,2-dimethyl-2*H*-chromene derivatives [[193-195](#_ENREF_193)]. Although several of the CMOFs were produced from the same linear ditiopic ligand, they possessed somewhat different catalytic properties due to their different 3D network structures as a result of being prepared in different-sized solvents such as DMF, diethylformamide (DEF), or dibuthylformamide (DBF). The frameworks with pcu topology were superior to those with higher porosity and larger open channel size in terms of substrate conversion, however, porosity and open channel sizes did not affect enantioselectivity and nearly the same ee values were observed.



**Figure 2.31**. Components leading to highly active ZnMOFs.

The catalytic activity of a series of metal-organic frameworks containing Jacobsen-type complexes **2.162**, bearing pyridyl struts, synthesized in the presence of zinc nitrate together with biphenyldicarboxylate (**2.163**) [[196](#_ENREF_196), [197](#_ENREF_197)] or tetracarboxylate ligands (**2.164**) [[197](#_ENREF_197), [198](#_ENREF_198)], were tested under the same, described above, catalytic conditions. In both cases the catalysts showed good efficiency and total turnover numbers reached nearly 4000 [[196](#_ENREF_196)]. Other manganese complexes have been embedded in MOFs using a ‘‘bottle around the ship’’ one-step encapsulation procedure which was applied to the amine functionalized MIL101(Al) framework (MIL – Materials Institute Lavoisier). This results in an effective catalyst in the epoxidation of dihydronaphthalene with *m*-CPBA/NMO system [[199](#_ENREF_199)]. In addition, amine-functionalized isoreticular MOF-3 (IRMOF-3) was used as a carrier support to incorporate a Mn(acac)2 complex in a post-functionalization strategy and catalytic efficiency of the catalyst obtained was studied in the epoxidation of alkenes using molecular oxygen [[200](#_ENREF_200)]. Moreover, a computational study investigated the influence of the steric effects of a metal-organic framework (MOF) on the enantioselectivity of manganese(III) salen epoxidation reactions using classical atomistic modelling [[201](#_ENREF_201)].

In summary, immobilization of catalysts on CPs and MOFs furnished results comparable to homogeneous conditions with the benefit of catalyst reuse over several consecutive runs. In addition, they offer the opportunity of incorporation of different catalytic sites in the same solid catalyst (e.g. Mn-salen and a Lewis acidic zinc centre).

## Manganese Complexes with Schiff-Base Ligands Immobilized on Organic Supports

An interesting feature of organic polymer-based supports is that they show higher stability to acid and basic media compared to traditional inorganic supports like alumina and silica, representing a potential disadvantage under some reaction conditions.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| *m*CPBA | H2O2 |
| **2.165** | conv 100%, ee 33% |  | homopolymer or copolymers of norbornene | [[202](#_ENREF_202)] |
| **2.166** | yield >99%, ee 35% |  | polymeric chiral Mn(salen) | [[203](#_ENREF_203)] |
| **2.167** | conv 92%, ee 46% |  | HEMA/DEGDMA | [[204](#_ENREF_204)] |
| **2.169** | - | conv 52.7%, selectiv 4.9% | PS/DVB | [[205](#_ENREF_205)] |
| **2.170** | - | conv 65.4%, selectiv 10.5% | PS/DVB | [[205](#_ENREF_205)] |
| **2.171** | yield 36% |  | PS/glass microfluidic channels (continuous-flow microfluidic reactor) | [[206](#_ENREF_206)] |

**Figure 2.32.** Modified organic supports.

Several studies have been carried out to modify organic supports with Jacobsen-type catalysts. The elegant examples are catalysts: (i) **2.165** (L = Cl) supported on homopolymer or copolymers obtained by ring-opening metathesis polymerization (ROMP) of norbornene monomers containing salen complexes anchored via a phenylene-acetylene linker [[202](#_ENREF_202)], and (ii) polymeric chiral salen Mn(III) complex with chiral diamine bridges (**2.166**) [[203](#_ENREF_203)]. The performance of these catalysts was habitually investigated in the asymmetric epoxidation of styrene. All catalysts gave excellent conversions, although enantioselectivities were modest, i.e. 32-35% ee for styrene oxide.

A series of immobilized catalysts **2.167** [[204](#_ENREF_204)] were also applied in the asymmetric epoxidation of styrene, and the highest activity was observed for the complexes immobilized on the (hydroxyethyl)methacrylate (HEMA) resins crosslinked with 3-mol% of diethylene glycol dimethacrylate(DEGDMA). The Mn(II) complexes of tridentate Schiff base ligands **2.169** and **2.170** [[205](#_ENREF_205)] were similarly examined in the catalytic oxidation of styrene, but the main reaction products were benzaldehyde, styrene oxide, and benzoic acid.

Supported catalysts show the potential to be used in continuous-flow processes and parallel synthesis. Mn(III)-salen **2.171** [[206](#_ENREF_206)] anchored onto a modified copolymer of styrene within glass microfluidic channels was applied in a continuous-flow microfluidic reactors to improve the efficiency of biphasic catalyst systems. The resulting system showed a 36% yield as a result of styrene oxide formation, which is similar to that in a macroscale environment, using a total volume of 2.1 µL at a flow rate 20 µL/min generating a residence time around 6.3 s. Moreover, under continuous conditions, a polyglycerol supported complex **2.168** [[207](#_ENREF_207)] was used as a homogeneous catalyst in the epoxidation of 6-cyano-2,2-dimethylchromene using *m*-CPBA/NMO. The total turnover number reached 80 in four repetitive batches, whereas using continuous operation in an ultrafiltration membrane reactor (MPF-50) it reached 240 for twenty residence times.

Less work appears to have been been devoted to chiral catalysts axially immobilized onto polymers. Nonetheless, the results obtained show that such heterogeneous salen catalysts exhibit high enantioselectivity as well as activity.



**Figure 2.33.** Polymer immobilised catalysts through axial ligation.

Jacobsen’s chiral catalyst and its phenylalaninol derivative were also immobilized by axial coordination onto cross-linked poly(hydroxyethyl methacrylate) (pHEMA). The resulting complexes **2.172** [[208](#_ENREF_208)] and **2.173** [[209](#_ENREF_209)] (Fig.2.33) were examined in alkene epoxidation reactions with NaOCl, and yielded the epoxides in moderate to good yield. For instance, styrene oxidation using the **2.172**/NaOCl/NH4OAc system resulted styrene oxide in 65% yield and 65% ee[[208](#_ENREF_208)], whereas -methylstyrene epoxidation under **2.173**/NaOCl/NH4OAc/[bmim]PF6 conditions gave the desired product in 92% yield and 91% ee [[209](#_ENREF_209)]. In addition, these catalysts could be recycled at least seven times without significant loss of catalytic activity.



**Figure 2.34.** Other polymer immobilized catalysts.

Another manganese(III) catalyst **2.174** (Fig.2.33) was immobilized onto a chitosan membrane, and it was tested in both monophasic and biphasic conditions, because the chitosan membrane acts as a catalytic barrier between two disparate phases: an organic substrate phase (substrate) and an aqueous solution of terminal oxidant. In general, the biphasic catalytic system was more actve in the epoxidation of the cyclooctene and styrene substrates with *m*-CPBA and TBHP, than monophasic solution (MeCN) [[210](#_ENREF_210)]. For example, styrene oxidation resulted in a 16% yield of epoxide in the biphasic system, but only 12% in MeCN solution. Moreover, Mn(salen) complexes **2.175** [[211](#_ENREF_211)] (Fig.2.34) were encapsulated in a polydimethylsiloxane (PDMS) based membrane using TBHP and tested in the oxidation of linear alkanes, 1,2-dimethylcyclohexane, and toluene to the corresponding alcohols, ketones or aldehyde.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Styrene oxide (the best conv/yield) | | Matrix | Ref. |
| *m*CPBA | Mukaiyama conditions |
| **2.176** | yield 98%, ee 38% | - | PAMAM-G1 | [[212](#_ENREF_212)] |
| **2.177** | - | conv 91%, selectiv 52%, ee 5% | Davisil-HD-G3 | [[213](#_ENREF_213)] |

**Figure 2.35.** Dendrimer supported catalysts.

Some studies have been carried out with chiral Mn(salen) complexes axially grafted onto a series of dendrimer supports with different generations of dendric polyamidoamines (PAMAM) (**2.176**, Fig.2.35 – G: generation) [[212](#_ENREF_212)] and onto PAMAM dendrimer functionalised silica (mesoporous silica gel Davisil grade 643 and non-porous silica Aerosil 200) (**2.177**) [[213](#_ENREF_213)]. The use of first generation PAMAM dendrimer-supported complex **2.176** resulted in an improvement of yield and enantioselectivity of the epoxidation of selected olefins, but the efficacy of **2.177** strongly depend on the type of support, i.e. **2.177** immobilized on the Aerosil(LD) induced greater enantioselectively, than embedded on Davisil(HD).

In addition, Jacobsen’s catalyst supported on mesoporous phenolic resin through direct axial coordination [[214](#_ENREF_214)] showed good catalytic activity and enantioselectivity in the epoxidation of 1,2-dialin by sodium hypochlorite as oxidant.

### Conclusion

Recently, there has been a growing interest in the use of polymer-based materials to immobilize catalysts, but the field is not as extensive as that of inorganic supports. Different polymers (swellable and soluble) as well as the method of immobilization (encapsulation, axial and covalent embedding) have been investigated with encouraging results, especially in styrene oxidation. The heterogeneous catalysts thus obtained usually display activities and enantioselectivities for the asymmetric epoxidation of olefins that are comparable to reactions using non-supported catalysts.

# Immobilized Manganese Complexes with Porphyrin Ligands

Porphyrins are naturally occurring, macrocyclic molecules containing four nitrogen atoms, one in each pyrrole ring, which act as tetradentate chelating ligands to make complexes with metals [[215](#_ENREF_215)]. Synthetic metalloporphyrins, especially iron and manganese porphyrin complexes, have been found to be one of the most worthwhile options for biomimetic catalysis and they have been used as a chemical models of the cytochrome P450-dependent monooxygenases, i.e. metalloenzymes which catalyse the selective oxidation of a variety of organic compounds, including hydrocarbons, using dioxygen [[216](#_ENREF_216)]. A wide range of substituted porphyrins have been synthesised and tested in epoxidation and hydroxylation reactions (including asymmetric oxidation) using PhIO, NaOCl, molecular oxygen, hydrogen peroxide, alkylhydroperoxides, potassium monopersulfate and others [[217-219](#_ENREF_217)]. However, the application of metal porphyrin complexes as homogeneous catalysts has some limitations related to their low-yielding synthesis as well as stability during reactions and possibility of reuse. These issues could be partially overcome by immobilization of the catalysts on different solid supports such as silica, alumina, carbon, layered anionic exchangers [[220](#_ENREF_220)], resins and MOFs. The heterogenisation of metalloporphyrins on surfaces include different methods like: (i) formation of typical covalent bonds e.g. in esters [[221](#_ENREF_221)] and amides; (ii) coordination bonds between a manganese centre and the support [[222](#_ENREF_222), [223](#_ENREF_223)]; (iii) encapsulation, electrostatic interactions and other non-covalent immobilization; (iv) incorporation of porphyrin moieties into metal organic framework (MOF) materials [[224](#_ENREF_224)].

Despite there being a few reviews published in recent years on the application of various metalloporphyrins in different reactions [[225](#_ENREF_225)], as well as supported counterparts [[26](#_ENREF_26), [28](#_ENREF_28), [226-229](#_ENREF_226)], neither of them focus only on manganese complexes in catalytic oxidation reactions.

## Manganese Complexes with Porphyrin Ligands Immobilized on Inorganic Supports

### Manganese Complexes with Porphyrin Ligands Immobilized on Silica-Based Supports via Covalent Bonding (C-C, C-N, C-S, C-O)



|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | Cyclooctene oxide (the best conv/yield) | | | | Matrix | Ref. |
| PhIO | NaIO4 | UHP | Oxone |
| **3.1** | - | - | - | yield 68% | MCM-41 | [[221](#_ENREF_221)] |
| **3.1**(X=amine) | - | - | conv 70%, selectiv 100% | - | SBA-15 | [[230](#_ENREF_230)] |
| **3.3** | - | conv 100%, selectiv 100% | - | - | HMS | [[232](#_ENREF_232)] |
| **3.7** | yield 71% | - | - | - | silica | [[235](#_ENREF_235)] |

**Figure 3.1**. Surface modified porphyrin systems.

One of the types of binding that has been employed to attach porphyrins onto solid supports is through the formation of the covalent bonds between the surface and the modified porphyrin. One such example was found in the deposition of *meso*-tetra-4-carboxyphenylporphyrinatomanganese(III) acetate on silica. Although, the Oxone/**3.1**/MCM-41 catalytic system was only effective in the epoxidation of cyclooctene (epoxide yield 68%) [[221](#_ENREF_221)], much better results were obtained by UHP (urea hydrogen peroxide) in the presence of the same metalloporphyrin anchored via an amide bond on amine modified SBA-15 [[230](#_ENREF_230)]. The similar approach was applied to immobilize manganese(III) 5, 10, 15, 20-tetrakis (4-methoxycarbonylphenyl) porphyrin (catalyst **3.2**, Fig. 3.1) [[231](#_ENREF_231)] as well as 5-(4-carboxyphenyl)-10,15,20-triphenyl porphyrin (catalyst **3.3**, Fig. 3.1) [[232](#_ENREF_232)]. The oxidation reactions carried out using NaIO4 and embedded on HMS (hexagonal mesoporous silica) catalyst **3.3** [[232](#_ENREF_232)] were reasonably productive (Fig. 3.1) in cyclooctene epoxidation. The catalytic activity of catalyst **3.2** supported on silica was tested in the oxidation of ethyl benzene and high selectivity (up to 99.9%) and good stability towards acetophenone in the absence of solvent using TBHP was obtained [[231](#_ENREF_231)]. The porphyrins heterogenized by the polymerisation of allyloxy porphyrin (5-(4-allyloxy)phenyl-10,15,20-tri(4-chlorophenyl) porphyrin (APTCPP)) with thiol functionalised SiO2 microspheres [[233](#_ENREF_233), [234](#_ENREF_234)] (**3.4**-**3.6**, Fig. 3.1) were evaluated for the hydroxylation of cyclohexane in the presence of molecular oxygen and ascorbate as a co-reductant, and the methyl substituted immobilized porphyrin **3.4** (R1=Me) showed higher catalytic efficiencies than **3.5** (R1=H) and **3.6** (R1=Cl) [[233](#_ENREF_233)]. In the oxidation of styrene, the supported tetrakis-4-azidephenyl substituted metalloporphyrin **3.7** was also examined, and styrene oxide was obtained in 47% yield [[235](#_ENREF_235)].



|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | Cyclooctene oxide (the best yield) | Matrix | Ref. |
| PhIO |
| **3.8** | 100% | HMS\_C16 | [[236](#_ENREF_236)] |
| **3.10** | 75% | montmorillonite(NH) | [[237](#_ENREF_237)] |
| **3.11** | 95% | silica(NH) | [[240](#_ENREF_240)] |
| **3.12** | 67% |

**Figure 3.2.** Covalently supported manganese porphyrin systems.

The manganese(III) and iron(III) complexes of modified 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin (Mn(TPFP)) were successfully covalently attached inside of the mesopores of hexagonal mesoporous silica with different pore size (HMS\_C12, HMS\_C16, **3.8**, Fig. 3.2) [[236](#_ENREF_236)], and examined in (*Z*)-cyclooctene and cyclohexane oxidation. The immobilized manganese catalysts were more effective in both oxidation reactions and showed comparable results to homogeneous counterparts. Other Mn(mTFPP) complex (**3.10**, Fig. 3.2) [[237](#_ENREF_237)] and manganese(III) 5, 10, 15, 20-tetrakis (pentafluorophenyl) porphyrin chlorides (Mn(pTFPP), **3.9**, Fig. 3.2) [[238](#_ENREF_238)] supported on modified montmorillonite K10 and silica gel were also tested in cyclooctene [[237](#_ENREF_237)], cyclohexane [[237](#_ENREF_237)], styrene [[237](#_ENREF_237)], and carbamazepine [[238](#_ENREF_238)] oxidation under similar conditions. Whereas, the complexes of mono-functionalised Mn(pTFPP) anchored on silica gel, polystyrene and montmorillonite K10 were tested in the oxidation of cyclooctane in the presence of air [[239](#_ENREF_239)]. The catalytic efficiency of other porphyrins covalently supported on silica i.e. manganese(III) 5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrin (Mn(PFTDCPP); **3.11**, Fig. 3.2) and manganese(II) 2,3,7,8,12,13,17,18-octachloro-5-(pentafluorophenyl)-10,15-20-tri(2,6-dichlorophenyl)-porphyrin (Mn(PFTDCCl8PP), **3.12**, Fig. 3.2) was also investigated in the oxidation of cyclooctene, cyclohexene, cyclohexane, and adamantane by PhIO and hydrogen peroxide [[240](#_ENREF_240)]. The higher epoxide yield in the epoxidation of cyclooctene was obtained using immobilized catalyst **3.8** and **3.11**.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | Cyclooctene oxide (the best conv) | | Matrix | Ref. |
| TBHP | H2O2 |
| **3.13** | 100% | 100% | silica(Br) | [[241](#_ENREF_241)] |

**Figure 3.3.** Complexes immobilized by quaternisation.

A manganese chlorin derivative was immobilized by the quaternarisation reaction of an amine in the chlorin backbone on a silica matrix to produce catalyst **3.13** (Fig. 3.3) [[241](#_ENREF_241)], which was utilised in the oxidation of *cis*-cyclooctene. The complex **3.13** exhibited slightly higher activity than its non-immobilized counterpart, and the substrate conversion reached up to 100% under oxygenating conditions. A similar approach was used to embed tetra-chloromethylphenyl-porphyrin (TMCPP) onto a copolymer of 4-vinylpyridine with styrene grafted on silica gel particles, and then after transformation to its corresponding manganese complex **3.14** (Fig. 3.2) [[242](#_ENREF_242)] applied in the oxidation of ethylbenzene to acetophenone with molecular oxygen without any co-reductant. In the hydroxylation of cyclohexane using iodosylbenzene has also been applied Mn(III) meso-tetrakis(2-pyridyl)porphyrin chloride (**3.15**, Fig. 3.3) [[243](#_ENREF_243)] and its 3-pyridyl and 4-pyridyl substituted isomers, anchored on chloropropyl-functionalized mesoporous silica SBA-15. These catalysts (**3.15**(2-py), **3.15**(3-py), **3.15**(4-py)) gave better overall yield than cationic metalloporphyrins supported on SBA-15 by electrostatic interaction.

### Manganese Complexes with Porphyrin Ligands Immobilized on Silica-Based Supports via the Complexation of the Manganese Metal Centre

The methodologies for metal complex immobilization usually depend on the surface chemistry of the supports. In this section, certain examples of catalytic properties of coordination complexes with different axial ligands, such as pyridine [[223](#_ENREF_223), [244](#_ENREF_244)] and imidazole [[245-247](#_ENREF_245)], will be presented. Incorporation of an axial nitrogen ligand often has a favourable effect on the stability and activity of metalloporphyrins (as well as previously mentioned salens), but also shows axial *bis*-ligation of the catalyst [[248](#_ENREF_248)].



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Porphyrin** | **Immobilized ligand** | Cyclooctene oxide (the best yield) | Matrix | Ref. |
| NaIO4 |
| Mn(R4P)Cl\_IGOPS | imidazole | 74% | silica | [[246](#_ENREF_246)] |
| Mn(TPP)Cl | 100% | silica | [[247](#_ENREF_247)] |

**Figure 3.4.** An axially ligated manganese porphyrin supported on silica.

Metallated by Mn(OAc)2, tetraphenylporphyrin (TPP) was immobilized on pyridine functionalised nanoporous silica (MCM-48) obtained via a sol-gel process. The catalytic activity of catalyst **3.16** (Fig. 3.4) was tested in cyclohexene oxidation using urea hydrogen peroxide [[223](#_ENREF_223)], and the best epoxide yield reached 87%. The application of colloidal silica was also investigated, but a lower conversion was obtained. Mn(TPP) was also immobilized in the same manner through supports obtained in the graft polymerisation of 4-vinylpyridine and styrene on modified silica (P(4VP-co-St)/SiO2) [[244](#_ENREF_244), [245](#_ENREF_245)], but its catalytic activity was demonstrated in ethyl benzene oxidation using dioxygen. Other manganese(III) complexes with *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (R4P) and *meso*-tetraphenylporphyrin (TPP) were immobilized on imidazole modified silica with short (–(CH2)3-, IPS) and longer (–C(OH)CH2O(CH2)3-, IGOPS) spacers [[246](#_ENREF_246)]. The supported catalyst with the IGOPS spacer gave satisfactory results in the epoxidation of alkenes such as cyclooctene, cyclohexene, and styrene using NaIO4/imidazole. Octabromotetraphenylporphyrinato-manganese(III)chloride (Mn(Br8TPP)Cl) and Mn(TPP)Cl [[247](#_ENREF_247)] were also supported onto imidazole modified silica gel, and their activity explored in the epoxidation of typically tested alkenes. The best results were obtained for cyclooctene epoxidation with NaIO4 (and Oxone), besides ultrasonic irradiation was more effective than magnetic strirring. Reuse of the immobilized Mn(Br8TPP)Cl catalysts in seven cycles resulted in only small decreases of activity and cyclooctene epoxide was obtained with 94-96 % yield in the 7th cycle. These effective catalysts were also explored in hydroxylation reactions of simple alkanes. Mn(TPP)Cl was also grafted via axial ligation by propylamine, sulfonic acid and thiol functionalised SBA-15 [[249](#_ENREF_249)] and the catalysts obtained were used in the catalytic oxidation of limonene. The efficiency of the heterogeneous systems was significantly better than those provided by unsupported porphyrins.

### Manganese Complexes with Porphyrin Ligands Immobilized on Silica-Based Supports via Noncovalent Interactions

Selected metallotetraphenylporphyrins adsorbed on MCM-41 obtained in a modified sol–gel process were explored in cyclohexene oxidation using H2O2. The highest conversion (26%) was observed for iron porphyrins, with good cyclohexanol selectivity (46%) observed for iron and manganese complexes, whereas the highest turnover number (1.54 x 105) was seen for Mn(TPP)Cl/MCM-41 [[250](#_ENREF_250)]. In addition, manganese tetraphenylporphyrin grafted onto Au/SiO2 [[251](#_ENREF_251)] acted as an active catalyst for the aerobic oxidation of cyclohexane, and oxidation products were obtained with good selectivity but poor overall yield of only ca. 5%. APTES modified manganese(III) 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (Mn(5-CTPP)) was immobilized in hollow SiO2 microspheres, synthesised by removal of Fe3O4 cores from silica coated-metalloporphyrin functionalised magnetite material [[252](#_ENREF_252)]. Its catalytic performance was tested in ethylbenzene oxidation resulting in modest substrate conversion of up to 16% in the first run (reducing to 12% by the sixth cycle) but with good acetophenone selectivity, which was essentially maintained throughout (75% in the first run and 72% in six consecutive cycles). In addition, metalloporphyrin (Mn(5-CTPP)) used in ethylbenzene oxidation could also be encapsulated in nanocages of mesoporous hollow silica spheres [[253](#_ENREF_253)].



|  |  |  |  |
| --- | --- | --- | --- |
| **Porphyrin** | Cyclooctene oxide (the best yield) | Matrix | Ref. |
| PhIO |
| **3.17** | 70% | silica (SGB) | [[254](#_ENREF_254)] |
| **3.17** | 15% | silica-Fe3O4 | [[257](#_ENREF_257)] |
| **3.18**(OAc) | 84% | silica-Fe3O4 | [[257](#_ENREF_257)] |
| **3.19** | 88% | silica-Fe3O4 | [[257](#_ENREF_257)] |
| **3.18**(Cl) | 77% | silica\_IPG | [[261](#_ENREF_261)] |
| **3.21** | 100% | silica\_IPG\_SO3 | [[261](#_ENREF_261)] |
| **3.22** | 94% | silica\_IPG\_SO3 | [[262](#_ENREF_262)] |
| **3.23** | 91% | silica\_NMe3 | [[262](#_ENREF_262)] |
| **3.23** | 97% | Amberlyst | [[262](#_ENREF_262)] |

**Figure 3.5.** Electrostatically grafted metalloporphyrins.

The neutral manganese porphyrin **3.17** [[254](#_ENREF_254)] (Fig. 3.5) was electrostatically grafted onto silica, and then studied in cycloalkanes oxidation [[254](#_ENREF_254), [255](#_ENREF_255)]. The highest yield was observed in the epoxidation of cyclooctene using the manganese catalyst deposited on silica synthesised through the sol-gel process in basic media (SGB) [[254](#_ENREF_254), [255](#_ENREF_255)]. The same porphyrin, **3.17**, but also cationic metalloporphyrins [[256](#_ENREF_256)] **3.18** (L = OAc), **3.19**, and **3.20** [[257](#_ENREF_257)] (Fig. 3.5), were immobilized on silica-coated Fe3O4 nanoparticles obtained by a sol-gel process. The catalytic activities of the solid catalysts were tested in the oxidation of selected alkenes and cyclohexane using iodosylbenzene (PhIO) as the oxygen donor. Application of iron catalyst **3.19** furnished comparable results to those obtained in the manganese **3.18** catalysed reactions. The cationic manganese porphyrin **3.18** (L = Cl, Fig. 3.5) was also grafted onto aluminated mesoporous silica SBA-15 (AlSBA-15) via ion exchange binding [[258](#_ENREF_258)], Al,Si-mesoporous molecular sieves [[259](#_ENREF_259)], MCM-41 [[260](#_ENREF_260)] and zeolite [[260](#_ENREF_260)]. These catalysts exhibited non-identical catalytic activity in the oxidation of cyclohexene with PhIO, and pentaacetate complex of **3.18** encapsulated on MCM-41 showed the highest efficiency and yielded epoxide with 98% selectivity and 91% overall yield [[260](#_ENREF_260)]. In addition, the same porphyrin **3.18**(L = Cl) [[261](#_ENREF_261)] and other cationic manganese(III) porphyrins **3.21** [[261](#_ENREF_261)], **3.22** [[261](#_ENREF_261), [262](#_ENREF_262)] (Fig. 3.5) were also attached on sulfonatophenyl (silica\_SO3), imidazole (silica\_IPG), and both sulfonatophenyl and imidazole (silica\_IPG\_SO3) modified surfaces, while the anionic sulfonatophenyl modified porphyrin **3.23** [[262](#_ENREF_262)] was grafted onto trimethylamonium (silica\_NMe3) substituted silica. In the oxidation of cyclooctene with PhIO, using the most effective catalyst, porphyrin **3.21**-silica\_IPG\_SO3 [[261](#_ENREF_261)], the yield of cyclooctene oxide reached 100%. In the oxidation of cyclohexane the same calalyst furnished virtually only cyclohexanol (69% yield), whereas **3.22**-silica\_IPG\_SO3 [[261](#_ENREF_261)] gave a higher overall yield, but with a 6:1 A:K ratio. In addition, **3.23** and **3.22** embedded on ion-exchange resins, especially **3.23**-Amberlyst, showed high catalyst reusability [[262](#_ENREF_262)].

The other cationic porphyrin **3.24** (Fig. 3.5) was encapsulated [[263](#_ENREF_263)] in pure mesoporous Si-MCM-41 and modified Al, Ti and V-MCM-41 molecular sieves with various Al/Si, Ti/Si, V/Si ratios [[264](#_ENREF_264)]. Their catalytic efficiency was examined in the epoxidation of styrene [[265](#_ENREF_265)] and cyclohexene with PhIO as oxygen source [[264](#_ENREF_264)]. Although, manganese grafted catalysts yielded moderate results giving styrene oxide in up to 37% yield and cyclohexene oxide in up to 30.3% yield formation, they were more selective and more efficient towards epoxidation than unsupported analogues [[264](#_ENREF_264), [266](#_ENREF_266)].

### Manganese Complexes with Porphyrin Ligands Immobilized on other Inorganic Supports

Subsequently, methods of immobilization were extended beyond silica supports using magnetic nanoparticles, silica and polymer coated magnetite nanoparticles, carbon and others.

**Table 3.1**. The catalytic efficacy of selected manganese complexes with porphyrin ligands immobilized on other inorganic supports

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Porphyrin** | Immobilization method | Cyclooctene oxide (the best conv/yield) | | Matrix | Ref. |
| PhIO | *n*-Bu4NHSO5 |
| **3.9** | covalent | yield 93% | - | silica\_Fe3O4 | [[267](#_ENREF_267)] |
| **3.9**(L = OAc) | covalent | - | conv 79%  selectiv 100% | silica\_Fe3O4 | [[268](#_ENREF_268)] |
| Mn(MeO-TPP)OAc | axial coordination | - | conv 88.5%  selectiv 100% | silica\_Fe3O4 | [[269](#_ENREF_269)] |

The catalytic efficiency of the pentafluorophenylporphyrin catalyst **3.9** [[267](#_ENREF_267)] (Fig. 3.2, Table 3.1) anchored on silica MCM-41 modified magnetite (Fe3O4) with two different pore sizes was studied in (*Z*)-cyclooctene and cyclohexane oxidation by PhIO. The catalysts exhibited higher activity in the epoxidation of (*Z*)-cyclooctene (yield up to 93%, Tab. 3.1), than in the oxidation of cyclohexane to cyclohexanol (yields 12-29%). In the precence of the similar metalloporphiryn **3.9** (L = OAc, Fig. 3.2) [[268](#_ENREF_268)] anchored on APTES modified Fe3O4@SiO2 nanoparticles through the amino propyl linkage, but under different oxidizing conditions, cyclooctene oxide was prepared with a lower yield (79%). The methoxy-substituted tetraphenylporphyrin Mn(MeO-TPP)OAc [[269](#_ENREF_269)] immobilized in an axial fashion by imidazole linker was also tested in alkene epoxidation [[268](#_ENREF_268), [269](#_ENREF_269)] and alkane hydroxylation using *n*-Bu4NHSO5 [[268](#_ENREF_268)].



**Figure 3.6.** Manganese porphyrin covalently supported on magnetite nanoparticles.

The manganese(III) complex of tetra-pyridyl modified porphyrin was also attached in a quaternerisation reaction to silica coated magnetite material (**3.25**, Fig. 3.6) and studied in the oxidation of alkanes and epoxidation of alkenes using NaIO4 [[270](#_ENREF_270)]. Although, catalyst **3.25** was effective in the oxidation of selected alkanes (51-72% yield), epoxidation of olefins occurred with higher yields (57-97%; cyclooctene oxide 97%).



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Porphyrin** | Axial ligand | Cyclooctene oxide (the best yield) | | Matrix | Ref. |
| NaIO4 | *n*-Bu4NHSO5 |
| **3.26** | propylamine | - | 89% | silica\_Fe3O4 | [[222](#_ENREF_222)] |
| Mn(TPP)Cl | imidazole | 98% | - | silica\_Fe3O4 | [[271](#_ENREF_271)] |

**Figure 3.7.** Manganese porphyrin supported on magnetite nanoparticles via amine linkers.

The partially brominated manganese–porphyrin was anchored through an aminefunctionality onto magnetic nanoparticles (Fe3O4) coated with a silica layer (Fe3O4@SiO2,catalyst **3.26**, Fig. 3.7) [[222](#_ENREF_222)], and tested in the oxidation of olefins and saturated hydrocarbons in water using *n*-Bu4NHSO5 as the oxygen source. A wide range of substrates was examined including cyclooctene, which was obtained with good yield. The metalloporphyrin Mn(TPP)Cl embedded on the same support (Fe3O4@SiO2) through an imidazole was also used as a catalyst in the epoxidation of selected substrates including cyclic olefins (e.g. cyclohexene), linear olefins (e.g. hept-1-ene), styrene and limonene in aqueous solution and with NaIO4 as an oxidant [[271](#_ENREF_271), [272](#_ENREF_272)], and the highest yield of 98% was obtained in the epoxidation of cyclooctene [[271](#_ENREF_271), [272](#_ENREF_272)]. The same strategy for the immobilization of Mn(TPP)OAc on functionalized magnetic nanoparticles utilising a pyridine group, gave catalyst **3.27** (Fig. 3.7), which was evaluated in the oxidation of cyclohexene using UHP [[273](#_ENREF_273)]. Good conversion (about 84%) and selectivity for epoxide formation (83%) were observed.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Porphyrin** | Cyclooctene oxide (the best yield) | | Matrix | Ref. |
| PhIO | aerobic cond. |
| **3.30** | 94% | - | silica\_Fe3O4 | [[276](#_ENREF_276)] |
| Mn(TCPP)Cl | - | 96% | Fe3O4\_tartaric acid | [[279](#_ENREF_279)] |

**Figure 3.8.** Magnetite nanoparticles coated with silica grafted manganese porphyrins.

Metalloporphyrins **3.28**-**3.30** (Fig. 3.8) explored in hydrocarbon oxidation were also grafted onto silica-coated Fe3O4 nanoparticles (**3.28**) [[274](#_ENREF_274)], Fe3O4-SiO2 mesoparticles (**3.29**) [[275](#_ENREF_275)], and Fe3O4-SiO2 mesoporous submicrospheres (**3.30**) [[276](#_ENREF_276)]. The use of nanoparticles modified with Mn(TPP) complex **3.28** as a catalyst in the oxidation of cyclohexane by PhIO led to the formation of cyclohexanol with moderate yield (17-20%) [[274](#_ENREF_274)]. Moreover, in catalytic cyclohexane oxidation, as well as epoxidation of cyclooctene using PhIO as the oxidant, several other Fe3O4-SiO2 materials were verified. For example, the yield of cyclooctene oxide reached 94% (827 TON) in the presence of the Fe3O4-SiO2-**3.30** manganese(III) catalyst [[276](#_ENREF_276)]. Additionally, in the oxidation of cyclohexane this catalyst gave a mixture of ketone and alcohol with moderate overall yield. In styrene oxidation [[275](#_ENREF_275)], a 10-fold increase of the turnover number (up to 462) in the first catalytic cycle was obtained using **3.29** porphyrin embedded on Fe3O4-SiO2 mesoparticles in comparison to its homogeneous counterpart. Porphyrins grafted onto magnetite nanoparticles coated with a polymer obtained by the co-polymerisation of an acrylate modified Mn(TPP) porphyrin with styrene [[277](#_ENREF_277), [278](#_ENREF_278)] were also examined in cyclohexane hydroxylation. These catalysts were more active than their homogeneous counterparts and resulted in a TON of 920 in the 1st and 945 in the 5th catalytic cycle [[277](#_ENREF_277)]. The manganese complex of tetra(4-carboxyphenyl)porphyrin Mn(TCPP)Cl adsorbed onto magnetic nanoparticles stabilised with (2*R*,3*R*)-(+)-tartaric acid showed satisfying activity and high stability for enantioselective epoxidation of unfunctionalized olefins using molecular dioxygen in the presence of isobutyraldehyde as the stoichiometric oxidant [[279](#_ENREF_279)]. The highest enantiomeric excesses and epoxide selectivity (ca. 100%) were obtained in oct-1-ene and dodec-1-ene oxidation, whereas substituted styrenes furnished good conversions (100%) but moderate epoxide selectivities (47-100%) and enantioselectivities (20-84%). However, the results are valuable because there are not many examples of the use of immobilized porphyrins in enantioselective synthesis.



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Porphyrin** | Cyclooctene oxide (the best conv/ yield) | | | Matrix | Ref. |
| TBHP | H2O2 | NaIO4 |
| **3.31** | conv 10%, selectiv 100% | conv 100%, selectiv 100% | - | MWNTs | [[280-282](#_ENREF_280)] |
| **3.32** | - | - | yield 95% | MWNTs | [[284](#_ENREF_284)] |
| Mn(pTPFP)Cl | - | conv 38%, selectiv 100% | - | CMK-3 | [[285](#_ENREF_285)] |

**Figure 3.9.** Manganese porphyrins supported on MWNTs.

Metalloporphyrins were also successfully supported on multi-wall carbon nanotubes (MWNTs). The activity of immobilized porphyrin **3.31** [[280-282](#_ENREF_280)] (Fig. 3.9) and **3.32** [[283](#_ENREF_283), [284](#_ENREF_284)] towards the epoxidation or hydroxylation [[283](#_ENREF_283)] of several typically tested substrates was investigated. In general, the epoxidation of the olefins in the presence of **3.31** [[280-282](#_ENREF_280)] resulted higher epoxide selectivities (70-100%) using hydrogen peroxide in the presence of imidazole, acetic anhydride under ultrasonic irradiation (US) [[280](#_ENREF_280)], than *tert*-butyl hydroperoxide as oxidant [[281](#_ENREF_281)] (12-21%). Only cyclooctene oxide was obtained with 100% selectivity in both cases, but with much better substrate conversion (100% vs 10%) under the first set of conditions. Besides, oxidation of alkenes using **3.32** and NaIO4 resulted in the formation of the corresponding epoxides with moderate to good yield (e.g. cyclooctene oxide 95%) [[284](#_ENREF_284)]. In the same reaction, the metallo(pentafluorophenyl)porphyrin Mn(pTPFP)Cl (see Fig.3.2) grafted on nanostructured carbon CMK-3 [[285](#_ENREF_285)], resulted in good epoxide selectivity but low conversion in three subsequent cycles using H2O2/NH4OAc. In contrast reaction in the presence of non-immobilized catalysts reached 98% conversion.



|  |  |  |  |
| --- | --- | --- | --- |
| **Porphyrin** | Cyclooctene oxide (best yield) | Matrix | Ref. |
| PhIO |
| **3.33** | 84% | LDH | [[286](#_ENREF_286)] |
| **3.33** | 20-30% | silica |
| **3.34** | 71% | LDH |
| **3.34** | 15-32% | silica |
| Mn(pTPFP) | 75% | alumina | [[287](#_ENREF_287)] |

**Figure 3.10.** Sol-gel immobilized metalloporphyrins.

Glycol porphyrins **3.33** and **3.34 were i**mmobilized on silica or on layered double hydroxide (LDH) [[286](#_ENREF_286)] were employed in (*Z*)-cyclooctene and cyclohexane oxidation in the presence of PhIO. As Fig. 3.10. shows, the catalysts supported on LDH were more effective (71-84% yield) than when the complexes were anchored on silica (15-32% yield). The related porphyrin Mn(pTPFP) entrapped in an alumina matrix [[287](#_ENREF_287)] resulted in up to 75% yield of cyclooctene oxide using PhIO. The catalyst **3.33**-LDH employed in cyclohexane oxidation resulted in 16% yield of the corresponding alcohol. Similar results were obtained in the presence of the manganese 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin (Mn(TNPP)OAc) grafted on boehmite, kaolin, ZrO2, Zr(OH)4, and ZnO [[288](#_ENREF_288)].



**Figure 3.11.** Manganese porphyrin monolayers.

Octadecyloxyphosphonic acid derivatives of Mn(TPFP) porphyrin were adsorbed as a monolayer film onto hydrophobic glass slides modified by a combination of Langmuir-Blodgett octadecylphosphonic acid (ODPA) and zirconium(IV) layers. In the epoxidation of *cis*-cyclooctene using iodosylbenzene, the supported porphyrin **3.35** showed an enhanced activity relative to non-supported catalysts, forming epoxide with 20-30% yield (893-1340 TON) compared to 4-15% yield (180-750 TON) for the non-immobilized systems [[289](#_ENREF_289)].

|  |  |  |  |
| --- | --- | --- | --- |
| **Porphyrin** | Cyclooctene  oxide (best yield) | Matrix | Ref. |
| PhIO |
| Fe-**3.36**Mn-**3.17**  Fe-**3.36**  Mn-**3.17** | 95%  70%  56% | halloysite | [[290](#_ENREF_290)] |
| Mn-**3.36** | 78% | kaolinite | [[292](#_ENREF_292)] |



**Figure 3.12.** Immobilized metalloporphyrins through electrostatic interactions.

The next example of heterogenisation of a porphyrin is the immobilization of its ionic form on several different clays, including halloysite [[290](#_ENREF_290)], montmorillonite [[291](#_ENREF_291)], and kaolinite. The ionic **3.17** (Fig. 3.5 and 3.12, pyridyl chloride salt) [[257](#_ENREF_257), [290](#_ENREF_290)] and Fe-**3.36** (Fig. 3.12, A = H) [[290](#_ENREF_290)] complexes were separately and simultaneously supported on a halloysite mineral clay [[290](#_ENREF_290)]. Application of supported Fe-**3.36-**Mn-**3.17** catalyst furnished a 95% yield of cyclooctenoxide and 39% of cyclohexane oxidation products (31% alcohol yield), which was significantly better than the results obtained using only one immobilized catalyst. However, manganese cationic forms of porphyrin **3.17** adsorbed on montmorillonite [[291](#_ENREF_291)], and Fe-**3.17**-Mn-**3.36** embedded on hydrozinicite/nanocrystalline anatase [[293](#_ENREF_293)] exhibited much higher activity towards oxidation of cyclohexane (80-82% alcohol yield). In addition, anionic metalloporphyrins Fe-**3.36** or Mn-**3.36** (A = Na, Fig. 3.12) supported on modified kaolinite [[292](#_ENREF_292)] were also tested in cyclooctene and cyclohexane oxidation under similar conditions and furnished the respective epoxide (Fig. 3.12) and cyclohexanol (yield 39%) with moderate yields.

### Conclusion

A wide range of immobilization techniques have been applied to embedding manganese porphyrin complexes onto inorganic supports, however, fewer examples of their preparation and use in hydrocarbon oxidation than immobilized salens have been reported. Neutral non-modified porphyrins e.g. manganese tertaphenylporphyrins Mn(TPP) were encapsulated into surface pores or supported via axial coordination on functionalised silica. The incorporation of functional group (Cl, N, COOH, allylO, ethynyl) into benzene rings of porphyrins allowed covalent anchoring of porphyrins onto surfaces, mainly on silica, magnetic nanoparticles and carbon. The cationic/anionic metalloporphyrins were encapsulated into mesoporous materials or deposited by ion exchange interactions. In hydrocarbon oxidation reactions, the conversions, yields and selectivities varied from low (ca. 10%) to very high (ca. 99%) depending on the hydrocarbon structure, terminal oxidant, type of metalloporphyrins, type of support and method of the preparation of the solid and the catalysts. Typically, covalently attached catalysts were tested in epoxidation/hydroxylation of alkenes, however the catalytic activity of several complexes e.g. **3.2**, **3.4**-**3.6**, **3.9** were verified in the oxidation of alkanes.

## Manganese Complexes with Porphyrin Ligands Immobilized on Hybrid Materials (Metal Organic Framework)

Metalloporphyrins [[294](#_ENREF_294)] have also been applied as organic linkers to build porous metal organic frameworks (MOFs) and often showed high catalytic activity in oxidation reactions due to their unique steric, electronic, and chemical properties [[295](#_ENREF_295), [296](#_ENREF_296)]. Moreover, ionic metalloporphyrins could be trapped within ionic MOFs.

The encapsulation of a cationic metalloporphyrin in (indium-imidazoledicarboxylate)-based *rho*-ZMOF, a negatively charged zeolite-type metal organic framework material, allowed the trapping of only one porphyrin molecule per cage. The free-base porphyrin was synthesized in reactions of In(NO3)3 with 4,5-imidazoledicarboxylic acid (H3ImDC) in the presence of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(p-toluenesulfonate) ([H2TMPyP] [*p*-tosyl]4) and then metallated with manganese [[297](#_ENREF_297)]. The formed catalyst was tested in cyclohexane oxidation in the presence of *tert*-butyl hydroperoxide (TBHP). As a result, cyclohexanol and cyclohexanone were obtained with 91.5% yield with a catalyst TON of 23.5.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Porphyrin** | Styrene oxide (the best results) | | Matrix | Ref. |
| PhIO | TBSIB |
| **3.37** | - | TON 605-1054 | MOF | [[298](#_ENREF_298)] |
| **3.38** | conv ˃99%, select 98% | - | MOF | [[299](#_ENREF_299)] |
| **3.38** | yield >99% | - | MOF | [[300](#_ENREF_300)] |
| **3.38**\_**3.43** | - | TON 2150 | MOF | [[304](#_ENREF_304)] |

**Figure 3.13.** Manganese porphyrins that have been incorporated into MOFs.

Different sized MOFs were prepared in the reaction of manganese(III)-porphyrin bis-carboxylic acid **3.37** (Fig. 3.13) with In(NO3)3 at various reaction times [[298](#_ENREF_298)], and used in catalytic styrene epoxidation using TBSIB (2-(*tert*-butylsulfonyl) iodosylbenzene). Immobilization of the catalyst gave some advantages: (i) an increase of TONs and catalyst stability; (ii) it blocked self-degradation of the catalyst by oxo-bridge dimer formation; (iii) improved reusability without loss of catalytic activity (1st cycle TON = 888, 5th cycle TON = 885). Moreover, an influence of the size of MOF rods on the catalyst efficiency was observed and the TON decreased if the size of the MOF rods increased e.g. in styrene oxidation for the small rods (0.5 ±0.2 µm, obtained after 2 min at 120 °C) TON = 1054, for the biggest (3.6 ±1.2 µm, obtained after 60 min at 120 °C) TON = 605. Under analogous conditions a MOF, prepared by combining tetracarboxylated ligand **3.38** (Fig. 3.13) with a bulky ligand **3.43** and zinc nitrate, was used with TBSIB (2-(*tert*-butylsulfonyl) iodosylbenzene) and gave 2150 catalytic turnovers [[304](#_ENREF_304)]. The latter catalyst was also used in the hydroxylation of cyclohexane, where products were obtained with 20% yield. The manganese catalyst known as CZJ- 1 (CZJ - Chemistry Department of Zhejiang University) [[299](#_ENREF_299)] obtained in the reaction of manganese tetrakis(4-carboxyphenyl)porphyrin (Mn(TCPP), **3.38**, Fig. 3.13) with *N*,*N*’-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNI) and zinc nitrate, was also investigated in the epoxidation of styrene (Fig. 3.13) and cyclohexane. High selectivity and conversion in both reactions were observed. In the oxidation of cyclohexane and olefins manganese porphyrin **3.38** (L = Cl, Fig. 3.13) was also examined, which was utilised in other metalloporphyrinic framework materials in the presence of zinc or cadmium nitrate. The catalyst exhibited excellent activity towards styrene oxide, however, moderate yield (20.6%) for cyclohexane oxidation products being observed using PhIO [[300](#_ENREF_300)].

TBHP oxidant was applied in the oxidation of alkylbenzenes to ketones using: i) metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin (Mn(H8OCPP)Cl, **3.39**, Fig. 3.13) and manganese(II) chloride (ZJU-18, ZJU – Zhejiang University) or cadmium chloride (ZJU-20) [[301](#_ENREF_301)] and ii) metalloporphyrin-based porous coordination polymers consisting of **3.40** (Fig. 3.13) and metal (Mn, Fe, Co, Ni, Cu, Zn) acetates. Although, high conversions (>99%) were obtained in the oxidation of ethylbenzene to acetophenone using **3.39**-ZJU-18 these were much lower in the oxidation of 4-ethylbiphenyl, suggesting that the MOF is a substrate size-selective catalyst. In addition, the **3.39**-ZJU-18 demonstrated good recyclability and high catalytic activity after 15 cycles, whereas the homogeneous catalyst lost its activity after 3 runs. The catalysts including **3.40**-MOF (MnII-**3.40-**MnII) [[302](#_ENREF_302)], 3.41-MOF (MnIII-**3.41-**metalII), and **3.42**-MOF (MnIII-**3.42-**metalII; metal: Mn, Co, Ni) [[303](#_ENREF_303)] exhibited noticeably lower activity, and acetophenone was obtained with high selectivities (up to >99%) but moderate ethylbenzene conversions (71-82%).

Overall, MOF catalysts have often been more effective than homogeneous catalysts, and sometimes more active than other heterogeneous catalysts (e.g. zeolites) [[297](#_ENREF_297)]. However, oxidation reactions which occur inside the pores of MOF are usually substrate size-selective, giving a small substrate scope range.

## Manganese Complexes with Porphyrin Ligands Immobilized on Organic Supports



**Figure 3.14.** Organic polymer supported manganese porphyrins.

Modified resins based on polystyrene matrices are convenient supports for the immobilization of a wide range of molecules due to the commercial availability of many supports possessing different swelling properties and anchoring groups, including Argogel (PEG grafted PS), Merrifield (PS/DVB) and Wang (PS/DVB with 4-alkoxybenzyl chloride linker) resins. These have been successfully utilised in the heterogenization of mono-functionalised manganese tetrakis(4-hydroxyphenyl)porphyrin, and explored in the epoxidation of typically selected olefins (e.g. cyclic and linear simple alkenes and styrenes) [[305](#_ENREF_305)] and dienes [[306](#_ENREF_306)]. The use of *p*-mono-functionalised Mn(TPP)Cl anchored onto Argogel [[305](#_ENREF_305)] and Merrifield resin [[305](#_ENREF_305)] (**3.44**, Fig. 3.14) resulted in poor to good epoxide yields (22-98%) in the first catalytic run, but significant diminishment in the catalytic activity was observed during reuse of the Argogel supported porphyrins, whereas the Merrifield anchored catalyst was stable. In the epoxidation of 7-methyl-1,6-octadiene, cyclooctadiene and limonene catalyst **3.44** anchored on Carboxy-Wang [[306](#_ENREF_306)] resin was found to be more active compared to simple Wang and Merrifield resins, and gave the desired mono-epoxides with 73-100% yields and the catalysts were stable over 4 runs. In an extension of this approach, utilising the peptide linker between the modified Wang resin and the mono-*O*-functionalised Mn(TPP)Cl the oxidation of limonene was developed [[307](#_ENREF_307)]. The highest substrate conversion (85%) was observed for catalyst **3.45** when anchored on a support with histidine, which presumably acts as an axial ligand, boosting the activity and stability of catalyst. Catalysts **3.46** and **3.47** (Fig. 3.14) showed diminished activity and conversion 37% and 66%, respectively.

A manganese complex of hydroxy modified TPP, depicted in Fig. 3.43, was attached to alkylated polystyrene (**3.48**) [[308](#_ENREF_308)] and to styrene-methylacrylic acid copolymer microspheres (**3.49**) [[309](#_ENREF_309)], whereas methyl modified TPP was anchored on styrene-hydroxyethyl methacrylate (HEMA) copolymer microspheres (**3.50**) [[310](#_ENREF_310), [311](#_ENREF_311)] then all of them were used in the catalytic hydroxylation of cyclohexane with molecular oxygen [[309](#_ENREF_309)]. Complex **3.50** with [[310](#_ENREF_310)] and without [[310](#_ENREF_310), [311](#_ENREF_311)] further functionalisation of the remaining hydroxyl groups of the surface with *n*-octadecanoic acid were also examined in the epoxidation of cyclohexene using the catalyst-O2-isobutyraldehyde system [[311](#_ENREF_311)]. The products of the oxidation of cyclohexane, i.e. cyclohexanol and cyclohexanone, were obtained with the highest yield using catalyst **3.50** possessing functionalized hydroxyl groups (TON reached 149 in the first run), with the lowest TON found using the non-supported catalyst (TON 4.65) [[310](#_ENREF_310)], whereas, cyclohexene oxide was obtained with good yield (95%), which was comparable with the non-supported system [[311](#_ENREF_311)]. In addition, Mn(TPP)Cl, *p*-chlorophenyl as well as *p*-nitrophenyl substituted Mn(TPP)Cl attached directly through a phenyl ring on crosslinked polystyrene microspheres **3.51**-**3.53** (Fig. 3.14) were also examined in the hydroxylation of cyclohexane with molecular oxygen as oxidant [[312](#_ENREF_312)]. The best substrate conversion (45%), cyclohexanol selectivity and TON (4155) were achieved in the presence of the *p*-nitrophenyl functionalised porphyrin.

Chloromethylated PS/DVB copolymer was used in a quaternerization reaction to immobilize tetra(4-pyridyl)porphyrinato manganese(III) complex (PS/DVB-Mn(TPyP), an analogue of catalyst **3.24**, Fig. 3.6, supported on magnetic material) [[313](#_ENREF_313)]. The oxidation of alkenes with NaIO4 resulted in good to excellent conversions of 56-99% and the system was also active and moderately chemoselective towards the hydroxylation of alkanes, e.g. cyclooctane, cyclohexane and *cis*-decalin were converted to the corresponding ketones and alcohols with conversions in the range 65-75%, whereas adamantane oxidation gave only an alcohol product (37% yield). In the same reactions, 4-aminophenyl derived manganese(III) porphyrin covalently anchored on carboxymethylated polystyrene resin (poly(4-styrylmethylacylchloride)) was explored but its activity was lower than PS/DVB-Mn(TPyP) [[314](#_ENREF_314)].

Substituted poly(ethylene glycol) (PEG) was also a suitable organic support for covalent deposition of manganese(III) porphyrins [[315](#_ENREF_315)]. The synthesized catalysts **3.54** and **3.55** (Fig. 3.14) exhibited excellent catalytic performance in the epoxidation of alkenes e.g. cyclooctene and indene, with epoxide yields of up to 100% with good catalyst stability shown after up to 7 consecutive runs. In addition, a modified poly(acrylic acid) (PAA) was used as a support to anchor an amino functionalised manganese(III) porphyrin **3.56** through a covalent bond. The heterogenised catalyst was tested in alkene epoxidation but its iron counterpart gave better results [[316](#_ENREF_316)]. The natural biopolymers such as chitosan (CTS) were also applied in manganese(III) deuteroporphyrin chlorine (Mn(DPCl)) [[317](#_ENREF_317)] immobilization through reaction of amine and hydroxyl groups of the support with a propionic group of the modified porphyrin, and used in the catalytic aerobic oxidation of cyclohexane without any additives or solvent. As a result, ketone and alcohol products were obtained with low conversion (17%) but with high chemoselectivity (89%) and good reusability, with the supported catalyst giving better results than its unsupported analogue (conversion 10%). In addition, chitosan was proposed to act as co-catalyst through an intermolecular interaction with the propionic acid groups of Mn(DPCl) and the amino groups of chitosan. Manganese tetraphenylporphyrin (Mn(TPP)) [[318](#_ENREF_318)] immobilized on chitosan was also tested under similar conditions to oxidize cyclohexane but substrate conversion was below 2%, although better results were observed for iron and cobalt analogues (7% and 16% respectively). The Mn(TCPP) complex was supported onto porous and non-porous chitosan (CTS) and also used for the catalytic aerobic oxidation of cyclohexane. It was found that the porous surface was slightly more suitable and average yields obtained were marginally higher (11% vs 10%) [[319](#_ENREF_319)]. The catalytic activity of Mn(TPP)-CTS [[320](#_ENREF_320)] was also examined in the oxidation of toluene, and under the optimal conditions (195 °C, 0.6 MPa) benzaldehyde and benzyl alcohol were obtained with low conversion (6%) but good selectivity (96%). Mn(TPP) was also anchored on chitin (CTN) and cellulose (CLS) [[321](#_ENREF_321)], as well as on inorganic minerals including boehmite (BM) [[322](#_ENREF_322)]. Mn(TPP) supported on boehmite [[322](#_ENREF_322)] was examined in the catalytic aerobic oxidation of cyclohexane, and led to the formation of cyclohexanol and cyclohexanone with average substrate conversion of 12.1% over 9 reaction cycles 85.6% selectivity for alcohol and ketone, and average TON of 1.49 x 105.

The mono-amine functionalized Mn(pTPFP) anchored via a covalent bond on polystyrene, but also on silica and montmorillonite K10, as well as Mn(TMPyP) encapsulated in a zeolite, were investigated in oxyfunctionalization of cyclooctane with molecular oxygen and furnished yields of mixtures of ketone and alcohol of up to 6% [[239](#_ENREF_239), [323](#_ENREF_323), [324](#_ENREF_324)].

The encapsulation of manganese porphyrins in a polystyrene (PS) matrix is another effective method used to heterogenise catalysts. The manganese(III) complexes of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (Mn(TDCPP)Cl) and *meso*-tetraphenylporphyrin (Mn(MnTPP)Cl) immobilized in PS with different molecular weights (40 000, 200 000, and 230 000) were used as catalysts in oxidation reactions of styrene and -methyl styrene under various conditions [[325](#_ENREF_325)]. The metalloporphyrins anchored on PS possessing average molecular weight of 200 000 performed with the highest activity and gave epoxide products in good yields (37-95%) and conversions (42-99%), which depended on the porphyrin ligand, oxidant and the axial ligand. However, anchored catalysts showed low reusability and could only be used in one or two catalytic cycles.



**Figure 3.15.** Sulfonated manganese porphyrin that was embedded in ion exchange resin.

The **3.57**-NaIO4-imidazole [[326](#_ENREF_326)] heterogenized oxidizing system, where **3.57** (Fig. 3.15) is the sulfonated Mn(TPP) embedded on Amberlite IRA-400 ion exchange resin with a PS/DVB matrix was applied in the epoxidation of selected olefins under ultrasonic irradiation (US) as well as using traditional stirring. In the oxidation of typically selected alkenes, including simple cyclic alkenes, styrenes, stilbenes and limonene, great enhancements in substrate conversions and epoxide selectivity were observed when US was used. For example, for oxidation of -methyl styrene the yield increased from 37% to 95%, and selectivity from 34% to 93% [[326](#_ENREF_326)].

### Conclusion

Although polymers and resins offer the possibility of incorporating diverse types of linkers and spacers between the immobilized molecule and support, since their swelling properties give the opportunity of high penetration with different solvents, only a few examples of embedding of Mn-porphyrins on organic matrixes have been reported. The most popular approach of immobilization has been covalent anchoring on resins, however, metalloporphyrins have also been immobilized on soluble polymers (e.g. PEG), natural biopolymers (e.g. chitosan), and styrene derived microspheres using encapsulation and ion exchange interactions to good effect.

# Immobilized Manganese Complexes with Amine Ligands

The field of hydrocarbon epoxidation and hydroxylation in the presence of immobilized manganese complexes with nitrogen containing ligands has been captured by supported manganese(III)-salen and manganese(III) porphyrin complexes. However, some attempts have been made to embed manganese complexes with simple amine ligands including TMTACN (1,4,7-trimethyl-1,4,7-triazacyclononane) and bpy (2,2′-bipyridine). Several catalysts were discovered and published before the year 2000 and their citations are scattered over a number of reviews [[10](#_ENREF_10), [24](#_ENREF_24), [327](#_ENREF_327), [328](#_ENREF_328)].



**Figure 4.1.** Examples of manganese complexes of nitrogen containing ligands that have been immobilized.

The complex of manganese(II) acetate with the Schiff base linked pyridyl ligand was covalently anchored on a APTMS functionalized mixed oxides SiO2/Al2O3 nanosized (**4.1**, Fig. 4.1) and tested in the oxidation of ethylbenzene and cyclohexene using TBHP with different reaction media. Oxidation of ethylbenzene and cyclohexene gave mixtures of products, with the predominant products being acetophenone (selectivity up to 96%) and 2-cyclohexene-1-one (selectivity up to 95%), respectively, under solventless conditions [[329](#_ENREF_329)].

Besides, a simple manganese(II) bipyridine complex [Mn(bpy)2]2+ was grafted using a “ship-in-a-bottle” strategy on novel microporous anionic borate network (ABN) prepared by the copolymerization with a lithium salt of weakly coordinating anions Li[B(C6F4Br)4] with 1,3,5-triethynylbenzene [[330](#_ENREF_330)]. Its catalytic performance was then tested in the oxidation of styrene and gave substrate conversions in the range 100-98% (1st-3rd run) and styrene oxide selectivity 65% in the first run, and 81% in the second and third runs. These results were higher than for the reaction in the presence of the un-supported [Mn(bpy)2]2+ complex. However, the microporous polymer Mn-ABN without the bipyridyl ligand also exhibited catalytic activity and resulted in similar values to the un-supported catalyst [[330](#_ENREF_330)].

Another manganese oxotetranuclear cluster [Mn4O2(AcO)7(bpy)2](ClO4)·3H2O with bipyridyl ligand was grafted onto silica particles and i) subsequently surrounded by additional silica overlayers around the attached manganese complex or ii) treated under vacuum and high temperatures to give catalysts without silica-matrix overlayers [[331](#_ENREF_331)]. The surface embedded complexes without silica-matrix overlayers were characterised by high manganese leaching (46-53%) during epoxidation reactions of *trans*-stillbene, whereas catalysts with added overlayers exhibited high stability over six reaction cycles. The best results (conversion 97%, selectivity 97%, leaching of manganese 0.01%) were obtained for the manganese complex, in which stacking of overlayers was performed twice [[331](#_ENREF_331)].

The ligand possessing both a pyridyl group and phenol group was used to form a binuclear carboxylated bridged Mn(II)Mn(III) complex [[332](#_ENREF_332)] **4.2** (Fig. 4.1), and after supporting on silica by entrapment via a sol-gel process or adsorption on silica gel, its catalytic efficiency was explored in the epoxidation of selected olefins. Although, the results obtained for immobilized complexes were similar to those gained using un-supported catalyst **4.2**, and gave quite low cyclohexene and cyclooctene epoxide yields in the range 26-39% and 29-74%, respectively, the embedded catalysts could be recovered and used at least 6 times without any loss of catalytic activity [[332](#_ENREF_332)].

The well-known binuclear manganese complex (**4.3**, Fig. 4.1) that is active in the oxidation of alkenes in the presence of H2O2 as terminal oxidant has been used, but its application frequently requires the use of co-catalysts and co-ligands e.g. oxalate, ascorbic acid, glyoxylic acid methylester methyl hemiacetal or acetone as solvent [[333](#_ENREF_333), [334](#_ENREF_334)]. Its efficiency was also boosted under reaction condition by the *in situ* grafting of MnTMTACN onto carboxylic acid-modified supports, which caused transformation of the inactive form of the catalyst [(TMTACN)MnIV(*μ*-O)3MnIV(TMTACN)]2+ into more active dicarboxylate-bridged analogues [(TMTACN)MnIII(*μ*-O)(*μ*-RCOO)2MnIII(TMTACN)]2+. Typically, the supported co-catalyst was obtained through grafting of 2-(carbomethoxy)ethyltrimethoxysilane onto silica [[335-338](#_ENREF_335)] followed by ester hydrolysis, but other carboxylic compounds e.g. 4-(triethoxysilyl)benzoate and dihydroxyhydrocinnamic acid were also immobilized. Other supports e.g. various Al2O3 [[337](#_ENREF_337)], silica combined with titanium (Ti-SiO2), aluminum oxide (SiO2-Al2O3) [[335](#_ENREF_335)] and activated carbon [[336](#_ENREF_336)] were also applied. The *in situ* grafted MnTMTACN catalyst was examined in the oxidation of cyclooctene, styrene, 4-substituted styrenes and other alkenes. In *cis*-cyclooctene oxidation reactions it was noticed that a significant increase of total turnovers (TON 465, 61%:39% epoxide : *cis*-diol) could be achieved compared to the homogeneous system by the presence of valeric acid (TON 53, 51%:49% epoxide : *cis*-diol) [[337](#_ENREF_337)]. In addition, the efficiency of the embedded monomeric analogue of manganese catalyst **4.3** was compared with supported **4.3**. It was found, that the monomeric supported catalyst [(TMTACN)MnIV(OMe)3]+ was less active in the epoxidation of styrene and 4-substituted styrenes (Me, OMe, CN, CF3, vinyl), e.g. styrene oxide was furnished with higher TON in the presence of **4.3** on propanoic acid-modified silica (TON 515) than its monomeric counterpart (TON 287), however, in the both cases the epoxide selectivity was the same and reached 91% [[336](#_ENREF_336)]. Microkinetic modeling was also used to investigate the reaction mechanism of *cis*-cyclooctene oxidation in the presence of heterogeneous binuclear manganese complex **4.3**, and the theoretical calculations agreed with the experimental observations; H2O2 activation by the supported complex **4.3** was the rate determining step, but the deactivation of the catalyst was a crucial part of the oxidation mechanism [[339](#_ENREF_339)].

The MnTMTACN complex was also entrapped within biopolymer microspheres and used in the oxidative degradation of morin (2’,3,4’,5,7-pentahydroxy-flavone) using hydrogen peroxide [[340](#_ENREF_340)]. Various other supportrd nitrogen containing manganese complexes have also been tested in alkene epoxidation with H2O2 as the oxidant, including amides [[341](#_ENREF_341)], Schiff-base derivatives, such as a manganese(II) imine-hydrazide complex [[342](#_ENREF_342)], [MnIII(acac)3] with the 1,4-diazabutadiene complex [[343](#_ENREF_343)], and a manganese(II) catalyst obtained from diethylenetriamine and 1,3-diones [[344](#_ENREF_344)]. The manganese(II) amide complex immobilized into zeolites [[345](#_ENREF_345)] **4.4**, was active in the oxidation of nerol ((*Z*)-3,7-dimethyl-2,6-octadien-1-ol), and gave good substrate conversions (45-100%), and yielded epoxyalcohols with good selectivities (46-76%) and low enantiomeric excesses (3.0-4.2%).

In summary, immobilized manganese complexes with a broad range of nitrogen containing ligands have been shown to be effective catalysts in many fields. Different manganese complexes (e.g. with Schiff base ligands, MnTMTACN) immobilized onto the various solid supports (silica, carboxylic acid-modified supports, SiO2/Al2O3) have been successfully prepared and their catalytic efficacy in olefin and alkane oxidation evaluated and compared to their homogeneous analogues. These modular catalytic materials are widely applicable to a broad range of substrates and oxidative systems and can provide products with high stereoselectivity (65-97%) and conversion (45-100%) which in a number of cases also show good recyclability of the supported catalyst.

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