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# Heterogenization of Mn and Fe complex oxidation catalysts

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**Abstract**

Homogeneous Fe and Mn oxidation catalysts can be immobilized on silica, zeolites, clays, layered double hydroxides and polymers. In addition to the well-known porphyrin catalysts, there is increasing interest in complexes with non-planar ligands. Based on a selection of examples, this paper discusses heterogenization methods, and the effects of heterogenization on the catalytic activity. ©2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Manganese; Oxidation; Porphyrin; Phthalocyanine

## 1. Porphyrin and phthalocyanine catalysis

Many Fe and Mn compounds intervene in oxidation processes via one-electron redox reactions, as in the Haber–Weiss decomposition of peroxides, which produces free radicals. However, a Fe-containing enzyme such as cytochrome *P*-450 manages to perform highly selective alkane and alkene oxidations [1]. Understanding of these *P*-450 reactions grew during the eighties, with experiments on Fe and Mn–porphyrin model complexes. These compounds activate oxygen donors XO ($H_2O_2$, ROOH, PhIO) in a two-electron reaction to yield $Fe^{V}$(por) or, more correctly, $Fe^{IV}(por^{\cdot+})$ species.

$$Fe^{III}(por) + XO \rightarrow Fe^{IV}(por^{\cdot+})O + X \quad (1)$$

The latter Fe (or Mn) species perform stereospecific alkene epoxidations and alkane hydroxylations. The activity and stability of the porphyrin catalysts can be remarkably improved by the introduction of Br, Cl, F or other electron-withdrawing substituents [2]. However, the porphyrins are expensive and are not easily separated from the organic constituents of the reaction mixture. This has stimulated the study of the heterogenization of these catalysts by a variety of routes.

### *1.1. Heterogeneous porphyrin catalysts*

While the four equatorial coordination sites in a Fe or Mn–porphyrin are occupied by the nitrogen atoms of the porphyrin, electron-donating ligands such as pyridine and imidazole can bind to the axial positions. In many cases, this has a highly beneficial effect on the catalytic performance of the porphyrin [3,4]. If the axial ligand is covalently bound to a surface, the porphyrin complex can be immobilized via a coordinative interaction (Fig. 1a). Cooke and Lindsay Smith [5,6] and Miki and Sato [7] prepared a series of polymer and silica-supported porphyrins. Depending on the flexibility of the support, not only mono- but also coordinatively saturated bis-ligated complexes may be formed. Leaching experiments show that retention of the complex depends on the solvent, and also on the porphyrin structure and the support. For

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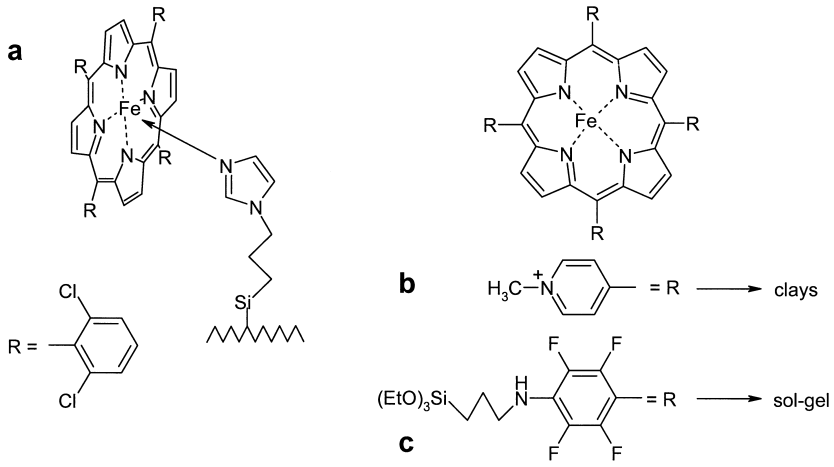



Fig. 1. Heterogenization of porphyrin complexes via (a) axial coordination of an immobilized base; (b) ion exchange; (c) sol–gel synthesis with a Si precursor.

instance, $Fe^{III}$–tetra(2,6-dichlorophenyl)porphyrin is firmly bound to imidazole-modified polystyrene, or to pyridine-modified silica.

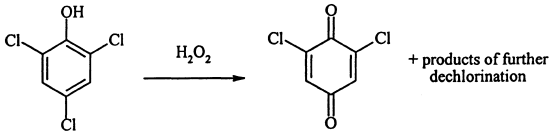
Ion exchange of cationic porphyrins is an obvious alternative route (Fig. 1b). Tetra(4-*N*-methylpyridyl) porphyrins easily bind to the weakly negative surface of unmodified silica [5], and particularly to true cation-exchangers such as montmorillonite clay, polyacrylate or sulphonated polymers [8–10]. In the intragallery space of the montmorillonites, and also on the polymers, the porphyrins can be highly aggregated. This implies that only a relatively small fraction of the complexes are available for catalysis.

Finally, Battioni et al. [11] have prepared porphyrins functionalized with organosilane groups (Fig. 1c). Such $(RO)_3Si$–por precursors can be used in a sol–gel process to give a solid with well-dispersed porphyrin complexes. An obvious advantage is that the siloxane matrix has a superior oxidative stability in comparison with organic polymers. This list of examples is of course not exhaustive, but illustrates well the different approaches that have been followed in the heterogenization of porphyrins.

### 1.2. Immobilization of phthalocyanines

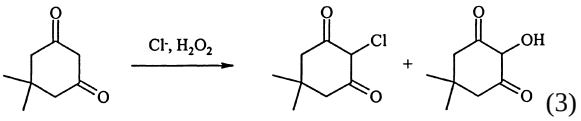
In spite of the structural differences between porphyrins and phthalocyanines, the catalytic properties in oxidation are to some extent similar. However, some phthalocyanines are easier to synthesize, and their oxidative stability is improved because they have nitrogen atoms at the *meso* position instead of C–H groups.

Ionic complexes, such as tetrasulphonated phthalocyanines (PcS), have been exchanged on strong basic anion exchanging polymers such as Amberlite IRA 900, or on inorganic anion exchangers such as layered double hydroxides (LDHs). The intercalation of PcS in LDHs is possible due to the large anion exchange capacity (up to $3\,\text{meq}\,g^{-1}$). The Co-containing PcS–LDH catalyst has been successfully used in the oxidation of phenols with $O_2$ as an oxidant [12]. Polymer-supported Fe or Mn sulphonatophthalocyanines have been applied in unusual reactions, such as the oxidative degradation of chlorinated phenols [13].




(2)

Additionally, similar systems have been used as models for chloroperoxidase. This implies phthalocyanine-catalyzed oxidation of $Cl^-$ to a '$Cl^+$' species, which subsequently reacts to chlorinate a nucleophilic substrate such as dimedone [14].



(3)

However, as $Cl^-$ is oxidized only with difficulty, the oxygenation of the dimedone substrate is an important side reaction.

The immobilization of phthalocyanines (Pc) in molecular sieves such as NaY, NaEMT or VPI-5 has been intensely studied [15–17]. The catalyst preparation is remarkably simple, with adsorption of dicyanobenzene and tetramerization by heating. The zeolite surface presumably plays a catalytic role in the numerous redox and acid–base reactions involved in the synthesis of the heterocycle. A more complex issue is the method used to introduce a metal ion in the phthalocyanine. When cation-exchanged zeolites are used, the chelation of the exchanged ion by the Pc is usually incomplete, and the residual, zeolite-coordinated metal ions may have undesired catalytic effects, such as the decomposition of the *t*BuOOH oxidant into $O_2$ and *t*BuOH. However, when an adsorbed metal complex such as ferrocene is used as a Fe source, all Fe is chelated by the phthalocyanines [18]. The resulting catalyst (FePc–Y) has been particularly successful in the oxidation of alkanes with *t*BuOOH as an oxidant. While the corresponding homogeneous catalysts are deactivated by bimolecular processes after a few turnovers, the site isolation in the zeolite-support increases the total turnover number to 6000 in the oxidation of cyclohexane with *t*BuOOH. The mechanism of this particular reaction has been studied, e.g. by determination of the kinetic isotope effect with $C_6H_{12}$ and $C_6D_{12}$ [19]. A further increase in turnover number can be achieved by introduction of electron-withdrawing nitro groups in the phthalocyanines, even if the concentration of $NO_2$-Pc in the zeolite is lower than for unsubstituted Pc [20].

There has been a persistent debate on the precise location of these zeolite-supported phthalocyanines. Based on electron microscopy, it has been claimed that the synthesis of phthalocyanines creates local defects in the zeolite structure [21]. Moreover, entrapment of phthalocyanines in a zeolite Y supercage seems to require deformation of the complex or of the zeolite cage. Whatever the precise mechanism of complex retention might be, there is no doubt that the association of the phthalocyanines with the zeolite produces a fully heterogeneous catalyst, with a much improved stability.

Detailed studies of the adsorption of reagents, products and solvents on the composite FePc–Y catalyst have revealed that polarity effects are particularly important. As the cyclohexane oxidation with *t*BuOOH proceeds, the polar products cyclohexanol and cyclohexanone adsorb in higher concentrations on the catalyst, and this progressively hinders the adsorption of fresh cyclohexane reactant [22]. Based on these ideas, a more advanced catalyst was designed, in which the FePc–Y zeolite is incorporated in a hydrophobic polydimethylsiloxane membrane. Thus not only the adsorption of the substrate around the active site is favored; the membrane design should also enable solventless reactions [19].

Finally, Balkus et al. [23] have immobilized Ru perfluorophthalocyanines inside faujasites by the so-called template method, in which the Pc complexes are dispersed in the synthesis gel. Even if the phthalocyanine concentration in the framework is rather low, acceptable yields of product per catalyst mass are obtained in the alkane oxidation with *t*BuOOH. This is due to the extremely high total turnover numbers for the entrapped Ru chelates.

## 2. Heterogeneous Mn or Fe catalysts with non-planar ligands

Following the extensive research on porphyrin catalysis in the eighties, attention gradually shifted to reactions catalyzed by Fe or Mn in a non-porphyrin environment. In biology, non-haem Fe and Mn intervene in an even more diverse series of oxido-reduction reactions than the porphyrin compounds. For instance, the active site in bacterial methane mono-oxygenase is a dinuclear Fe complex, with bridging hydroxide and acetate ligands [24]. Dinuclear Mn is the active center of catalase, while plants and algae use a tetranuclear Mn complex in the oxidation of water by photosystem II [25,26]. Other proteins with redox active Fe or Mn centers are hemerythrin, myohemerythrin, ribonucleotide reductase, fatty acid desaturase and aromatic dioxygenases [27–30].

In spite of this functional wealth in biology, there are relatively few metal complexes that are well established as homogeneous catalysts for selective hy-

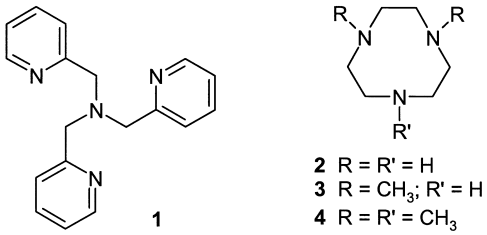



Fig. 2. Structures of (a) TPA (tris(2-pyridylmethyl)amine); (b) tacn; (c) dmtacn; (d) tmtacn.

droxylation or epoxidation. Among the ligands used by the group of Que and coworkers [27], particularly TPA (tris(2-pyridylmethyl)amine) has been studied in great detail (Fig. 2a). The Fe complex of this ligand apparently catalyzes the selective hydroxylation of alkanes with *t*BuOOH as an oxidant. In these reactions, several experimental observations point to a metal-mediated oxidation, such as the high kinetic isotope effect ($k_H/k_D = 10$), or the stereospecificity in the oxidation of *tertiary* alkanes [31]. However, it seems difficult to totally preclude free radical oxidation of the alkanes, due to the ability of the Fe–TPA complex to catalyze the Haber–Weiss decomposition of peroxides [32]. Conspicuously, there are hardly any results on the epoxidation of alkenes with this catalyst system. A preference for epoxidation over allylic oxidation of, e.g. cyclohexene would be a major indication for the predominance of metal-mediated oxidation.

### *2.1. Heterogenization of Mn–bipyridine complexes in zeolite Y*

The immobilization of Mn–bipyridine complexes in faujasite typifies the effects that site isolation and complex entrapment can have on the catalytic properties in oxidation. Depending on the nature of the charge compensating anions in solution, bis-complexes of Mn and two bipyridine ligands have a more or less ubiquitous tendency to decompose $H_2O_2$. The role of the anion is that it allows or precludes the formation of binuclear complexes. For instance, acetate is a bridging, binucleating ligand. However, when $[Mn(bpy)_2]^{2+}$ complexes are formed in zeolite Y by adsorption of bipyridine on Mn exchanged faujasite, the zeolite lattice itself functions as a charge compensating anion [33]. Moreover, one $[Mn(bpy)_2]^{2+}$ complex fits precisely inside one faujasite supercage, and this impedes the formation of dimeric complexes.

This faujasite-entrapped $[Mn(bpy)_2]^{2+}$ catalyzes the epoxidation of olefins with $H_2O_2$ as an oxidant [33]. The acid–base properties of the surrounding zeolite framework have a profound influence on the products obtained. With an X zeolite, the selectivity for the epoxide is high. However, zeolites Y with some residual Brönsted acidity catalyze epoxide ring opening with the formation of *trans* diols, such as *trans*-1,2-cyclohexanediol from cyclohexene. These diols are not stable to the reaction conditions, and further oxidation with an excess $H_2O_2$ leads to a product mixture containing the adipoin, the diketone and even the diacid.

### *2.2. Mn–triazacyclononane complexes: homogeneous catalysis*

1,4,7-Triazacyclononane (tacn) and related ligands are facially coordinating tridentate ligands (Fig. 2b–d). In 1:1 complexes with octahedral ions such as $Fe^{3+}$ or $Mn^{2+/3+}$, three coordination sites are available in positions *trans* to the three coordinating nitrogen atoms. In solution, these sites may be used to form bridges with neighboring metal–tacn units. With Mn and tacn in oxidative conditions, a tetranuclear complex with $Mn^{IV}{}_4O_6$ core is thermodynamically most stable, namely $[(tacn)_4Mn^{IV}{}_4O_6(Br)_{3.5}(OH)_{0.5}]\cdot 6H_2O$. With Mn and tmtacn (1,4,7-trimethyl-1,4,7-triazacyclononane), dimers are formed, e.g. $[(tmtacn)_2Mn^{III}{}_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2$ (Fig. 3). A large number of crystalline structures can be found in the detailed work of Wieghardt et al. [34] and Wieghardt [35].

Catalytic research into Mn–tmtacn was triggered by the observation that several Mn–tmtacn complexes are extremely active in the decomposition of $H_2O_2$ at relatively low temperature. This is highly important for fabric bleaching in laundry applications [36]. Moreover, it appeared that small amounts of organic substrates such as polyphenols, styrene, or vinylbenzoic acid could be oxidized under similar conditions, i.e. in an aqueous buffer containing $H_2O_2$ [37]. While peroxide decomposition is a desirable characteristic in the context of stain bleaching, it dramatically limits

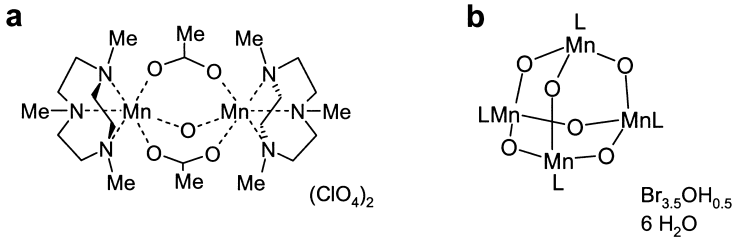
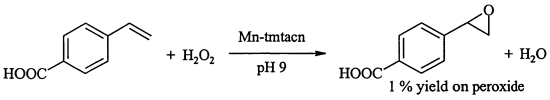


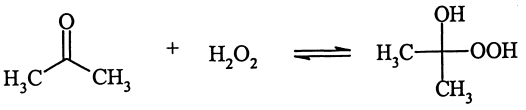

Fig. 3. Formation of polynuclear complexes with Mn and triazacyclononane ligands in solution: (a) dinuclear complex of $Mn^{III}$ and tmtacn; (b) tetranuclear complex of $Mn^{IV}$ and tacn (L).

yields on a peroxide basis if selective oxygen transfer to an organic substrate is the goal. Typically, about a 100-fold excess of $H_2O_2$ is required to epoxidize 1 equiv. of olefin.




(4)

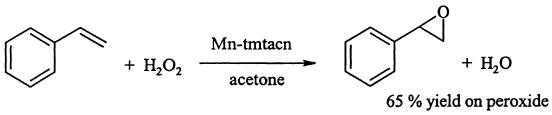
A first step to improve peroxide efficiencies in Mn–tmtacn catalyzed reactions is to work in a well chosen solvent [38]. In most solvents, such as methanol or acetonitrile, peroxide efficiencies are invariably below 5%. However, in acetone, yields based on peroxide are considerably improved, due to the formation of a perhemiketal between acetone and $H_2O_2$.




(5)

The perhemiketal is easily observed by NMR spectroscopy at 273 K, with a characteristic $^{13}C$ resonance at 113 ppm for C(OH)(OOH). As a result of this equilibrium, less free $H_2O_2$ is available for decomposition. On the other hand, one might not exclude that the perhemiketal itself coordinates on a Mn complex and transfers its active oxygen atom. However, due to the reversibility of reaction (5) and the high reactivity of the reaction mixture, such hypotheses are hard to prove directly.

During the epoxidation with Mn–tmtacn in acetone, the 16-line EPR signal of a magnetically coupled $Mn^{III}$–$Mn^{IV}$ dimer is observed, proving that in these conditions, formation of dimers is not precluded. The reaction protocol with Mn–tmtacn in acetone is particularly suitable for epoxidation of styrenes, in which $H_2O_2$ efficiencies up to 65% have been measured.




(6)

However, the reaction is not completely stereospecific for *cis* olefins, and free radicals may be formed if the reactivity of the olefin substrate is low. A similar protocol with acetone as a solvent has been adopted by Feringa and coworkers [39] for the Mn–tmtacn catalyzed oxidation of benzyl alcohols to benzaldehydes with $H_2O_2$.

A more efficient way to control the properties of Mn–tmtacn in homogeneous catalysis is the use of catalytic amounts of co-ligands. In the presence of 1,3-diketones, but particularly with carboxylic acids, strong effects on the catalysis have been observed. Some simple carboxylic acids, e.g. acetic acid or benzoic acid, inhibit the decomposition of $H_2O_2$ by Mn–tmtacn [40]. This agrees with the inhibitory effect of benzoic acid on the oxidation of benzylic alcohols [39]. However, other acids such as fumaric acid or oxalic acid improve the efficiency of the $H_2O_2$, while keeping the turnover rate high. Moreover, the acidity of the reaction mixture has an important effect on the rate and efficiency. With oxalic acid alone, the reaction is slow, but efficiencies are excellent (>95%). The reaction is fast with Na-oxalate as a co-catalyst, but this has a lower efficiency (Fig. 4). An almost ideal compromise is the use of 1.5 mol of Na-oxalate and 1.5 mol of oxalic acid per mole of Mn–tmtacn.

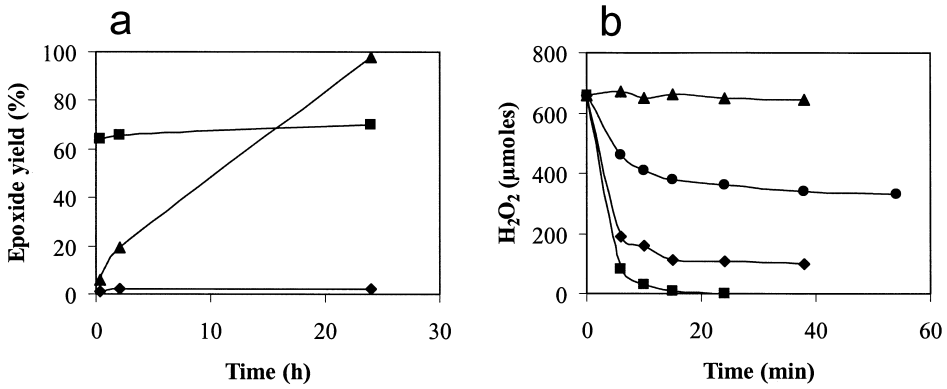
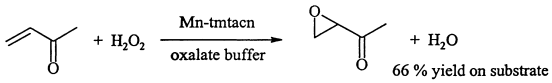



Fig. 4. Effect of oxalate co-ligands on (a) 1-hexene epoxidation; and (b) $H_2O_2$ disproportionation with Mn–tmtacn. ◆ — no co-ligand; ▲ — 3 mol oxalic acid per mole of Mn–tmtacn; ■ — 3 mol Na-oxalate per mole of Mn–tmtacn; ● — 1.5 mol of Na-oxalate and 1.5 mole of oxalic acid per mole of Mn–tmtacn. Conditions: (a) 1 mM Mn–tmtacn, 0.67 M 1-hexene, 1 M $H_2O_2$ in $CH_3CN$; (b) 1 mM Mn–tmtacn, 0.67 M $H_2O_2$ in 1 ml $CH_3CN$.

EPR spectroscopy suggests that before addition of the oxidant, Mn is in the trivalent state. Preliminary electron spray MS data indicate that in these conditions, a 1:1:1 complex of Mn, tmtacn and oxalate is formed. The main advantages of the Mn–tmtacn–oxalate procedure are: (i) strongly improved efficiency; (ii) full stereospecificity for epoxidation of *cis* or *trans* alkenes; (iii) stability of the epoxide in reaction conditions; and (iv) high activity, for instance 1000 turnovers within a few hours. Even electron-deficient olefins such as methyl vinyl ketone are easily epoxidized.




(7)

This suggests that the oxalate increases the electrophilicity of the Mn-activated oxygen atom, probably via electron-withdrawing effects. The dramatic improvement of the catalytic properties of Mn–tmtacn by addition of an oxalate buffer clearly illustrates the importance of controlling the occupation of the coordination sites *trans* to the ligand nitrogen atoms. While epoxidation with homogeneous Mn–tmtacn catalysts has been highly successful, the catalyst is apparently less suitable for alkane oxidation. For *tertiary* alkanes, such as *cis*-1,2-dimethylcyclohexane, stereospecific hydroxylation has been observed [41]. This suggests that free radicals may not be involved. However, with *secondary* alkanes such as cyclohexane, cyclohexyl hydroperoxide is a main product, together with the alcohol and the ketone [42]. The hydroperoxide most likely arises from reaction of a cyclohexyl radical with $O_2$. Hence an 'oxygen-rebound' mechanism, as proposed by Groves et al. [43] for alkane oxidation with porphyrins, is apparently not valid for alkane oxidation with Mn–tmtacn and $H_2O_2$.

### *2.3. Heterogenization of Mn–triazacyclononane complexes in zeolite Y*

Zeolite-exchanged transition metal ions can easily be chelated by adsorbed amine ligands. Cyclic amines such as tacn or its trimethylated analog tmtacn are sufficiently small and flexible to enter the pores of twelve-membered ring zeolites such as zeolite Y. The complexation of exchanged $Mn^{2+}$ (or $Cu^{2+}$) by adsorbed triamines can be followed by EPR or UV–Vis spectroscopy [44]. In the case of the reaction of MnNaY with tmtacn, a mono-nuclear $Mn(tmtacn)^{2+}$ complex is formed inside the zeolite pores, as can be inferred from the shift in the zero-field splitting in the EPR spectrum. Upon exposure to $H_2O_2$, a 16-line EPR signal of a dinuclear $[(tmtacn)Mn^{III}–X_3–Mn^{IV}(tmtacn)]^{n+}$ is observed ($X = O^{2-}$, $OH^-$). This proves that the mobility of the initially formed $Mn(tmtacn)^{2+}$ complexes is sufficiently high to allow formation of the same type of dimers as in solution. Importantly, such dimers

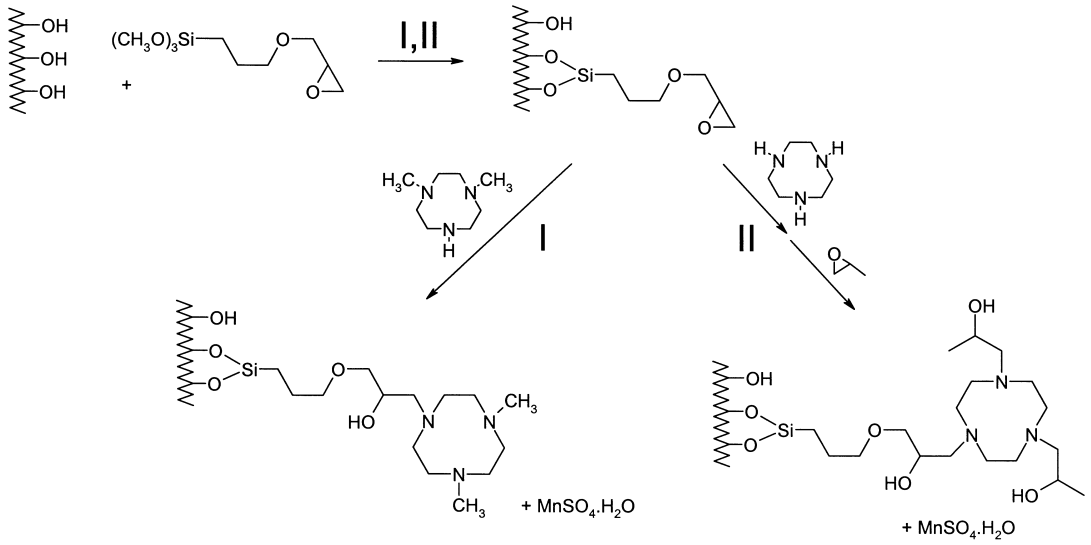



Fig. 5. Heterogenization of tacn-type ligands on $SiO_2$.

always retain a positive charge, which will improve their retention inside the cation-exchanging zeolite Y.

As can be expected based on the spectroscopic similarities, the catalytic properties of Mn(tmtacn)–NaY zeolites are very similar to those of Mn(tmtacn) in solution [45]. By far the best results are obtained in acetone, for instance in the epoxidation of cyclohexene or styrene with $H_2O_2$. The heterogeneity of the reaction was explicitly demonstrated by a filtration experiment, which showed negligible progress of the styrene reaction after removal of the catalyst. The small differences between the heterogeneous and the homogeneous reactions are mainly a matter of reaction selectivity. For instance, the stereoretention in the epoxidation of a *cis* alkene is generally higher with the zeolite-supported catalyst; with the zeolite, the selectivity for allylic oxidation in the reaction of cyclohexene is even smaller than with the homogeneous catalyst. A possible explanation for the latter phenomenon is that if any free radicals are formed, these are less likely to start chain reactions in a zeolite than in solution.

### *2.4. Heterogenization of Mn–triazacyclonane complexes via covalent linking*

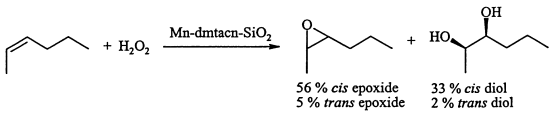
A second route for heterogenization of the Mn–tmtacn catalysis is to covalently anchor the ligand to a support material such as $SiO_2$, and to bind Mn to the heterogenized ligand (Fig. 5). When tmtacn reacts with a functional group such as haloalkyl or an oxirane group, its chelating properties are affected or even lost. Therefore, tmtacn itself cannot be used in the synthesis of a heterogeneous catalyst. Alternatively, we have used tacn or dmtacn (1,4-dimethyl-1,4,7-triazacyclononane; see Fig. 2c) [46,47]. If tacn is used (see route II in Fig. 5), the two remaining *secondary* nitrogen atoms must be alkylated, e.g. with propylene oxide, in order to obtain a catalyst with some activity. However, the hydroxyalkyl pendant arms in the catalyst prepared by route II can coordinate to the Mn, and this slows down the catalysis.

Better results have been obtained with dmtacn (Fig. 5, route I). This ligand already contains two *N*-$CH_3$ groups. The heterogenization via reaction with an immobilized glycidyl group alkylates the third nitrogen atom in the cycle. Consequently, the eventual immobilized ligand is structurally highly similar to the original tmtacn.

The results obtained with dmtacn on $SiO_2$ are far better than those with materials prepared via other routes [47]. For instance, Mn–dmtacn–$SiO_2$ catalyzes the epoxidation of mono-substituted olefins with $H_2O_2$. Turnover numbers of 200 mol of styrene epoxide per mole of Mn are reached within 3 h.

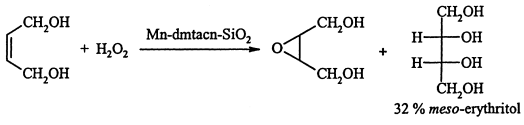
The reaction works equally well with rather unreactive terminal olefins such as 1-hexene. For these mono-substituted olefins, epoxide selectivities are mostly between 85 and 90%.

With disubstituted olefins and $H_2O_2$, the Mn–dmtacn–$SiO_2$ catalyst produces the epoxide as a main product (65–85%). However, sizable amounts of the *cis*-dihydroxylation product (15–35%) are formed as well [47].




(8)

These *cis* diols cannot arise from epoxide hydrolysis, as this would lead to a *trans* configuration. The Mn–dmtacn–$SiO_2$ reaction is therefore a direct, heterogeneous alternative to the classical reaction of olefins with toxic, volatile $OsO_4$. A potential and proven application of the Mn-catalyzed *cis*-dihydroxylation is the direct conversion of the cheap feedstock *cis*-2-buten-1,4-diol into the valuable polyol erythritol, without formation of the epimeric threitols.




(9)

However, increasing the diol over epoxide ratio in these reactions remains an important challenge.

The most plausible mechanism for the formation of the *cis* diols is depicted in Fig. 6. In a first step, Mn in its +III resting state reacts with $H_2O_2$ to form an active Mn–oxygen species. After the latter Mn–oxygen species adds on the olefin, a second oxygen atom, originating from coordinated water or hydroxyl ions (Y in Fig. 6), is inserted into the olefin. Such a formation of *cis* diols has never been observed with homogeneous Mn–tmtacn type catalysts. With dissolved Mn–tmtacn and co-ligands, the coordination sites *cis* to the activated oxygen are not accessible to, e.g. water. In the absence of co-ligands, dissolved Mn–tmtacn complexes form dimers, and consequently decompose $H_2O_2$. The spatial isolation of the Mn centers over the Mn–dmtacn–$SiO_2$ catalyst therefore seems an essential condition for the *cis* dihydroxylation.

### 2.5. Chiral heterogeneous oxidation catalysts

The substituted Mn–salen catalysts developed by Katsuki [48] and by Jacobsen effect an enantioselective oxygen transfer to prochiral olefins, with NaClO or with PhIO as a terminal oxidant. The initial claims that salen complexes may be entrapped inside zeolite Y raised the expectation of a facile heterogenization of this catalyst. Ogunwumi and Bein [49] designed a procedure to entrap Jacobsen's complex inside a hexagonal faujasite with EMT topology. A related approach was followed by Corma and coworkers [50], with zeolite Y as a host material, and with a sterically much less congested salen ligand. With both catalysts, the enantiomeric excess is to some extent preserved. In alternative approaches, modified salen ligands have been tethered to polymeric supports [51]. A principal shortcoming of these Mn–salen type catalysts is that their lifetime is rather limited, due to oxidative

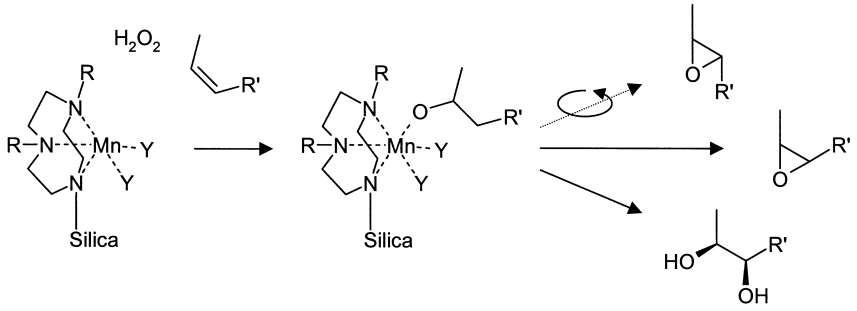
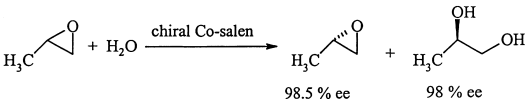



Fig. 6. Catalytic olefin oxidation with $H_2O_2$ and Mn–dmtacn–$SiO_2$. Insertion into the olefin of Mn-coordinated Y ($Y = H_2O$, $OH^-$) leads to a *cis*-diol.

destruction of the salen ligand. Additionally, only a limited number of substrates can be epoxidized with satisfactory enantiomeric excess. In comparison with the Mn–salen catalyzed epoxidation, the recently discovered hydrolytic resolution of epoxides with Co–salen compounds is a valuable alternative [52]. Indeed, the productivity of the Co–salen catalyst is much higher due to the absence of oxidants, and the procedure even gives excellent results for simple epoxides such as propylene oxide.




(10)

Besides this homogeneous catalyst, Jacobsen has also proposed a related heterogeneous catalyst in which the complex is bound via an ester linkage to commercial hydroxymethylpolystyrene beads. Such catalysts are of value not only in large scale processes, but also in the combinatorial, automated synthesis of libraries of new compounds [53].

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