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Fe-Catalyzed Oxidation Reactions of Olefins, Alkanes, and Alcohols: Involvement of Oxo- and Peroxo Complexes

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Abstract In this review, recent developments of iron-catalyzed oxidations of olefins (epoxidation), alkanes, arenes, and alcohols are summarized. Special focus is given on the ligand systems and the catalytic performance of the iron complexes. In addition, the mechanistic involvement of high-valent iron–oxo species is discussed.

Keywords Homogeneous catalysis · Iron · Oxidation

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1 Introduction

Iron is an essential element for the proper function of nearly all known biological systems. In living organism, iron is generally stored in the center of metalloproteins, most important is the incorporation into heme complexes. These complexes

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are an essential part of cytochromes, e.g., P450 cytochromes, which mediate numerous redox reactions, and of oxygen carrier proteins, for example hemoglobin. Nonheme iron-based enzymes include, for example, methane monooxygenase and hemerythrins, which regulate oxygen transport and fixation in marine invertebrates. The key active species in numerous biological oxidation reactions in which activation of oxygen is involved are known to be high-valent iron–oxo intermediates of heme and nonheme complexes [1, 2]. In the past two decades, significant advancements towards the direct characterization of Fe(IV)O-, Fe(V)O-, and even Fe(VI)O-species have been made [3]. Hence, detailed knowledge on the structure of model complexes such as $[Fe^{IV}(TMCS)(=O)](PF_6)$ (TMCS = 1-mercaptoethyl-4,8,11-trimethyl-1,4,8,11-tetraza cyclotetradecane) [4] and $Fe^{V}TAML(=O)$ (TAML = tetraamido macrocyclic ligand) [5] are nowadays available. There is no doubt that such basic knowledge is important for the understanding of biologically relevant actions and the more rational design of artificial catalysts. However, so far the catalytic performance of most of these model complexes is far away from the efficiency of biologically active systems and sometimes with model complexes no catalytic behavior is observed at all.

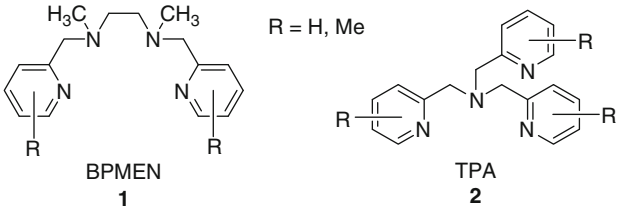
Because there exist a number of reviews which deals with the structural and mechanistic aspects of high-valent iron–oxo and peroxo complexes [6, 7], we focus in this report on the application and catalysis of iron complexes in selected important oxidation reactions. When appropriate we will discuss the involvement and characterization of Fe–oxo intermediates in these reactions.

2 Epoxidation of Olefins

Among the different oxidation reactions, both from an academic as well as industrial point of view, the epoxidation of olefins is of considerable interest [8, 9]. Subsequent ring opening reactions make epoxides versatile building blocks for large-scale materials, bulk, and fine chemicals as well as agrochemicals and pharmaceuticals [10]. Due to their low cost, benignancy to the environment and biological relevance, there is an increasing interest to use iron complexes as catalysts for epoxidation reactions [11, 12]. Notably, in addition to the catalysts, the applied oxidant determines the value of the oxidation system to a significant extent (for a list of common oxidants, their active oxygen contents and waste products see [13]). From ecological and economical points of view, molecular oxygen [14, 15] and hydrogen peroxide are the oxidants of choice with regard to waste and by-products.

As an example heme-models have been reported to catalyze the epoxidation of olefins to the corresponding epoxides in good yield [16, 17]. In particular, $[Fe^{III}(TPP)Cl]$ (TPP = 5,10,15,20-meso-tetraphenylporphyrin) was reported to oxidize naturally occurring propenylbenzenes to the corresponding epoxides up to 98% selectivity (conversion 98%) using H_2O_2 as oxidant [16]. The major drawback

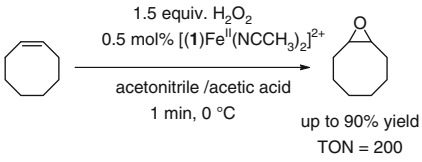
for these heme-model systems is the low tunability of the catalysts for different olefins. Mechanistic insights into the iron porphyrin-catalyzed epoxidation using hydrogen peroxide were published by Bell and coworkers [18, 19].



Scheme 1 BPMEN and TPA ligands for the iron-catalyzed epoxidation of olefins

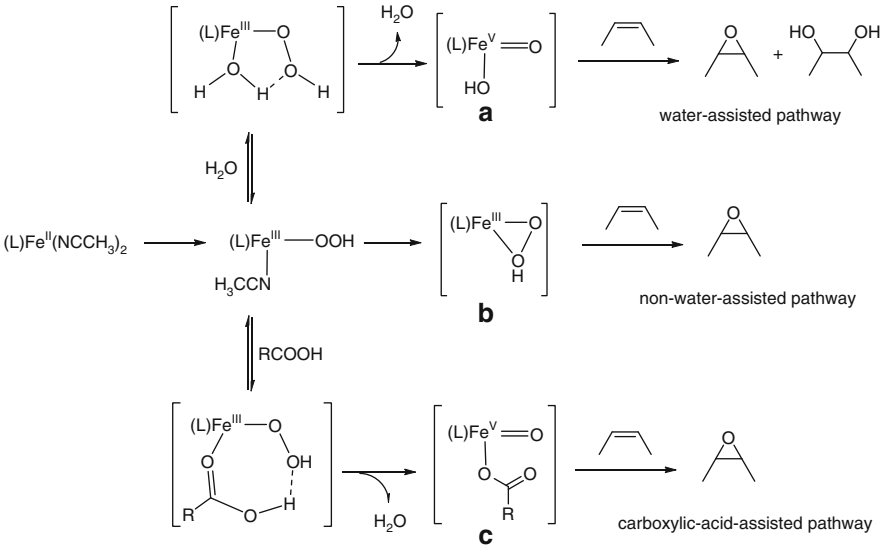
In addition, also nonheme iron catalysts containing BPMEN **1** and TPA **2** as ligands are known to activate hydrogen peroxide for the epoxidation of olefins (Scheme 1) [20–26]. More recently, especially Que and coworkers were able to improve the catalyst productivity to nearly quantitative conversion of the alkene by using an acetonitrile/acetic acid solution [27–29]. The carboxylic acid is required to increase the efficiency of the reaction and the epoxide/diol product ratio. The competitive dihydroxylation reaction suggested the participation of different active species in these oxidations (Scheme 2).

Scheme 2 Epoxidation of cyclooctene catalyzed by Fe(BPMEN) and Fe(TPA) complexes

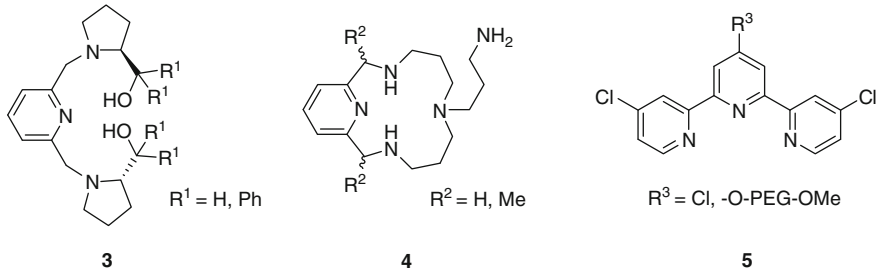


Mechanistic studies revealed a mononuclear Fe^{V}=O species (intermediate C, Scheme 3) to be most likely the epoxidizing agent in this catalytic epoxidation in the presence of acetic acid. In the absence of carboxylic acid, Fe^{III}–OOH and Fe^{V}=O (intermediates A and B, Scheme 3) were proposed as active oxidation species depending on the presence of water. This conclusion is mainly based on labeling studies and spectroscopic methods to identify the active species. The reported results are quite controversial to the results of the groups of Talsi and Comba. Talsi and coworkers reported the formation of an Fe^{IV}=O intermediate supported by NMR- and EPR-spectroscopy [30], which is in agreement with the results obtained by Comba and coworkers [31]. In addition, other groups explored similar high-valent iron–oxo species, which shed light on this catalytic mechanism [32, 33].

Iron complexes with the pentadentate ligand **3** derived from pyridyl and prolinol building blocks containing a stereogenic center were reported from the group of Klein Gebbink (Scheme 4) [34]. In alkene oxidations with hydrogen peroxide,



Scheme 3 Proposed mechanism of iron-catalyzed oxidation by Que and coworkers

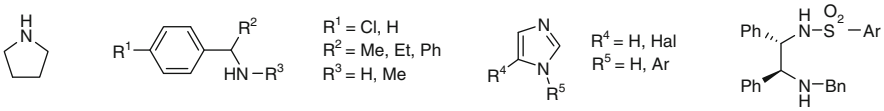


Scheme 4 Selected ligands for iron-catalyzed epoxidation of alkenes

the corresponding epoxide is obtained only in low yield as a racemic mixture. Moreover, the formation of the corresponding allylic alcohol and ketone is observed. The product ratio is influenced by the nature of the coordinating anions (Cl or OTf).

To mimic the square-pyramidal coordination of iron bleomycin, a series of iron (II)complexes with pyridine-containing macrocycles **4** was synthesized and used for the epoxidation of alkenes with H_2O_2 (Scheme 4) [35]. These macrocycles bear an aminopropyl pendant arm and in presence of poorly coordinating acids like triflic acid a reversible dissociation of the arm is possible and the catalytic active species is formed. These complexes perform well in alkene epoxidations (66–89% yield with 90–98% selectivity in 5 min at room temperature). Furthermore, recyclable terpyridines **5** lead to highly active Fe^{II}-complexes, which show good to excellent results (up to 96% yield) for the epoxidation with oxone at room temperature (Scheme 4) [36].

With respect to generality, it still remains challenging to discover iron-catalyzed epoxidations, which allow efficient and selective reactions for both aromatic and aliphatic olefins. A convenient and efficient method for the fast epoxidation of a variety of olefins was developed by our group. The simple and practical in situ catalyst system consists of iron trichloride hexahydrate, pyridine-2,6-dicarboxylic acid (H_2pydic), and an organic amine [37–39]. By modifying the organic amine almost all classes of olefins are accessible for epoxidation with hydrogen peroxide under mild conditions. Pyrrolidine **6** and benzylamine derivatives **7** turned out to be advantageous as coligands (Scheme 5). The development of a second generation catalyst in the absence of pyridine-2,6-dicarboxylic acid was achieved by using iron trichloride hexahydrate in combination with bio-inspired imidazole derivatives **8** [40, 41]. Selected results are shown in Table 1.



Scheme 5 Organic coligands used in the epoxidation of alkenes

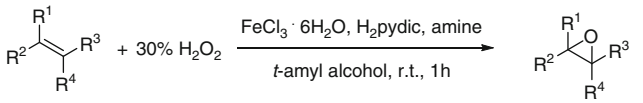
Until recently only few examples on asymmetric epoxidation using iron-based catalysts were reported in the literature (Scheme 6) [42–44]. With [Fe(BPMCN)$(CF_3SO_3)_2$] **10**, 58% of the epoxide with 12% *ee* was obtained in the oxidation of *trans*-2-heptene [42].

By elaborating 5,760 metal–ligand combinations, Francis and Jacobsen identified three Fe-complexes with peptide-like ligands, which gave the epoxide in 15–20% *ee* in the asymmetric epoxidation of *trans*-β-methylstyrene utilizing 30% H_2O_2. The homogeneous catalyst **11** derived from this study gave 48% *ee* with 100% conversion of *trans*-β-methylstyrene [43]. Aerobic epoxidation of styrene derivatives with an aldehyde coreductant catalyzed by tris(δ,δ-dicampholylmethanato) iron(III) complex **12** was also reported.

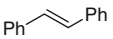
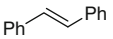
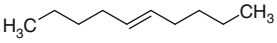
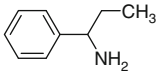
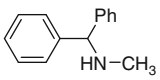
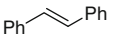
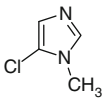
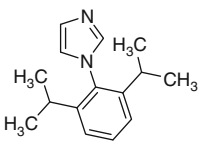
A breakthrough in iron-catalyzed asymmetric epoxidation of aromatic alkenes using hydrogen peroxide has been reported by our group in 2008. Good to excellent isolated yields of aromatic epoxides are obtained with *ee*-values up to 97% for stilbene derivatives using diphenylethylenediamines **9** as ligands (Scheme 5) [45, 46].

Additional recent ligand developments to be mentioned are the chiral bipyridine ligand **13** and the polypyridine ligand **14** (Scheme 7) [47, 48]. The μ-oxo-dinuclear iron complex of **13** performed the enantioselective epoxidation with peracetic acid in high conversion and yield. Unsymmetrical alkenes were oxidized with enantiomeric excess ranging from 9 to 63%, whereas symmetrical *trans*-stilbene led to racemic mixtures. The importance for the dinuclearity of the catalyst has been pointed out since the mononuclear complexes of the ligand showed lower rate, yield, and lower enantiomeric excess. Disadvantage of the reaction is the use of peracetic acid as oxidant which leads to significant amounts of acetic acid as

Table 1 Selected result of the epoxidation using iron trichloride hexahydrate, pyridine-2,6-dicarboxylic acid, and an organic amine

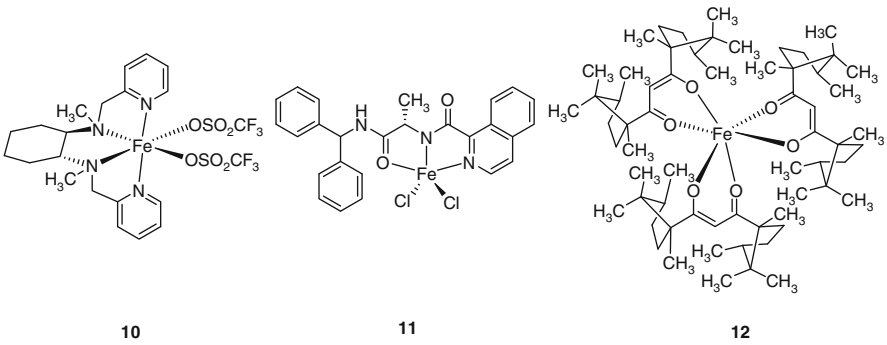


R^1, R^2, R^3, R^4 = H, aryl, alkyl

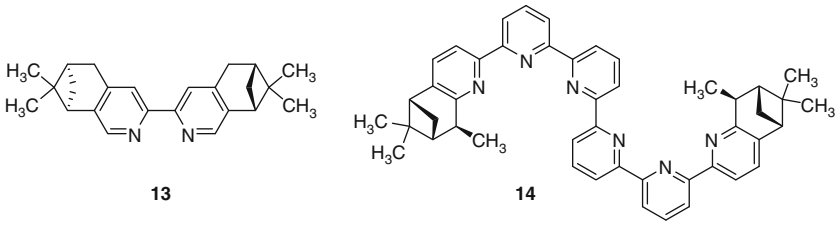
Entry	Substrate	Amine	Yield[a]
1			97
2			93
3			96
4			89
8[b]			87
9[b]			65

Reaction conditions: 5 mol% $FeCl_3 \cdot 6H_2O$, 5 mol% H_2pydic, 10–12 mol% amine, 3 equiv. H_2O_2
[a]Yield was determined by GC analysis;
[b]H_2pydic was omitted

by-product. Hence, acid labile epoxides are not accessible. The μ-oxo-dinuclear iron complex of **14** showed excellent reactivity and selectivity towards terminal and 1,2-substituted aromatic alkenes in the epoxidation with H_2O_2 in acetonitrile/acetic acid. Enantiomeric excess up to 43% was achieved.



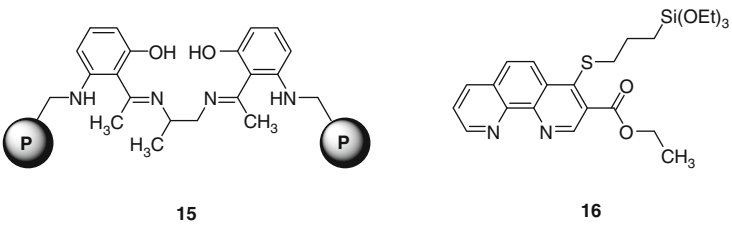
Scheme 6 Chiral iron complexes for the asymmetric epoxidation of olefins



Scheme 7 Recently reported ligands for iron-catalyzed asymmetric epoxidations

Asymmetric epoxidation systems using iron porphyrin heme-mimics are also known, however the labor-intensive and expensive syntheses is limiting their applications [49].

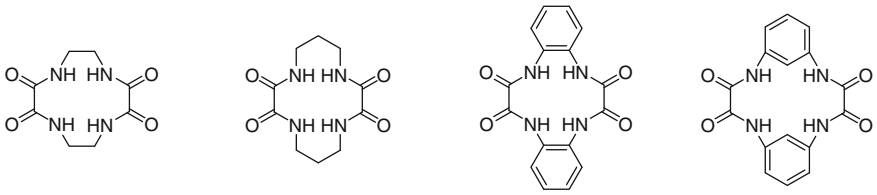
The immobilization of metal catalysts onto solid supports has become an important research area, as catalyst recovery, recycling as well as product separation is easier under heterogeneous conditions. In this respect, the iron complex of the Schiff base HPPn **15** (HPPn = *N*,*N*′-bis(*o*-hydroxyacetophenone) propylene diamine) was supported onto cross-linked chloromethylated polystyrene beads. Interestingly, the supported catalyst showed higher catalytic activity than the free metal complex (Scheme 8) [50, 51]. In terms of chemical stability, particularly with



Scheme 8 Immobilized HPPn and Stacks phenantroline ligand

regard to oxidizing conditions, inorganic matrices show improved stability [52–54]. Inspired by homogeneous [{Fe(phen)$_2$(H$_2$O)}$_2$ μ-O]$^{4+}$ (phen = 1,10-phenantroline), Stack and coworkers immobilized phenantroline derivative **16** on micelle-templated silica SBA-15 (Scheme 8) [55, 56]. The system showed more selective and efficient catalytic activity for olefin epoxidations with peracetic acid than the analogous homogeneous catalyst.

In addition, iron(II) complexes of tetraaza macrocyclic ligands **17–20** were encapsulated within the nanopores of zeolite-Y and were used as catalysts for the oxidation of styrene with molecular oxygen under mild conditions (Scheme 9) [57].



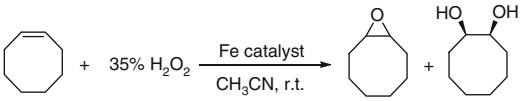
Scheme 9 Tetraaza macrocyclic ligands for supported iron catalysts

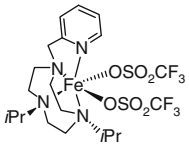
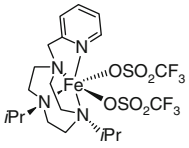
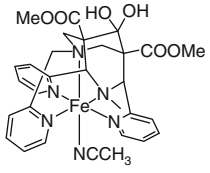
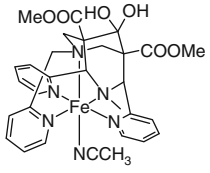
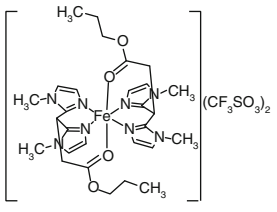
3 Dihydroxylations

1,2-Diols are applied on a multimillion ton scale as antifreezing agents and polyester monomers (ethylene and propylene glycol) [58]. In addition, they are starting materials for various fine chemicals. Intimately connected with the epoxidation-hydrolysis process, dihydroxylation of C=C double bonds constitutes a shorter and more atom-efficient route to 1,2-diols. Although considerable advancements in the field of biomimetic nonheme complexes have been achieved in recent years, still osmium complexes remain the most efficient and reliable catalysts for dihydroxylation of olefins (reviews: [59]).

So far, biomimetic and bio-inspired approaches mimicking the nonheme oxygenases have been studied with ligands such as the tetradentate N$_4$ ligand BPMEN **1** also named as mep or the tripodal ligand TPA **2** (reviews: [60–62], Scheme 1). Lately, TPA ligands were used also as model for NDO (naphthalene 1,2-dioxygenase), which catalyzes the conversion from naphthalene to *cis*-(1*R*,2*S*)-1,2-dihydro-1,2-naphthalenediol [63]. Another tetradentate N$_4$-ligand family was examined by Costas and coworkers in 2008 based on the methylpyridine-derivatized triazacyclononane (TACN) backbone. The resulting Fe^{II} complexes showed activity both in alkane hydroxylation (vide infra) and in olefin dihydroxylation [64]. For example, cyclooctene is oxidized under inert atmosphere with 35% hydrogen peroxide in the presence of catalytic amounts of different iron complexes to attain the corresponding epoxide and *cis*-diol in 19% and 62% yield, respectively, based on the oxidant (Table 2, entry 1). The unprecedented high water incorporation into the

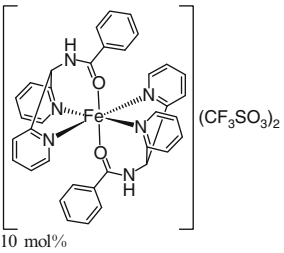
Table 2 Epoxidation of cyclooctene with iron catalysts and H_2O_2



Entry	Catalyst	Olefin:H_2O_2	Epoxide[a]	*cis*-Diol[a]	References
1[b]	 10 mol%	100:1	19	62	[64]
2[b]	 1 mol%	10:1	12	73	[64]
3[c]	 10 mol%	100:1	50	0	[29, 31]
4[b,c]	 10 mol%	100:1	10	10	[29, 31]
5	 10 mol%	100:1	28	11	[69]

(*continued*)

Table 2 (continued)

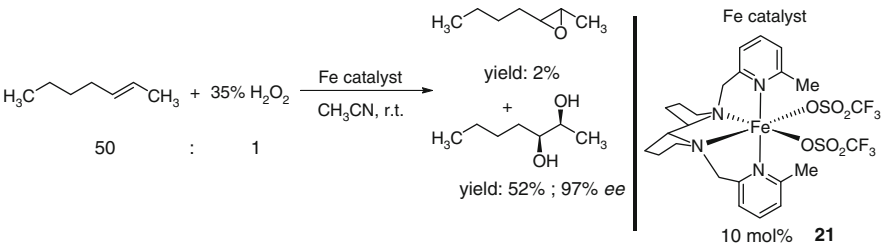
Entry	Catalyst	Olefin:H_2O_2	Epoxide[a]	*cis*-Diol[a]	References
6		100:1	5%	70	[70]

[a]Yield based on the limiting reagent
[b]Reactions carried out in inert atmosphere
[c]The corresponding anions were not mentioned

corresponding epoxides and diols was later explained by a substrate-dependent interplay between two isomerically related high-valent iron oxo species [65]. Further improvements were achieved using a pentadentate N_5-ligand motif known as bispidine ligands [29, 31]. This Fe^{II} complex catalyzed the oxidation of cyclooctene with hydrogen peroxide mainly to afford the epoxide as product. However, under anaerobic conditions *cis*- and *trans*-1,2-diols are observed (Table 2, entries 3 and 4).

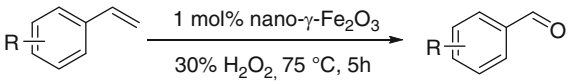
In a specific subset of the nonheme iron oxygenases including the Rieske dioxygenases, the mononuclear iron(II) center is coordinated by the so-called 2-his-1-carboxylate triad [66]. This ligand scaffold has emerged as a versatile platform for oxidative transformations and as a fundamental model for the design of new ligands. For example, Klein Gebbink and coworkers introduced bis(1-alkylimidazol-2-yl)propionates as a new tridentate, tripodal N, N, O ligand family [67], which were applied as model of the active site of the extradiol cleaving catechol dioxygenases [68] and as epoxide/dihydroxylation catalysts mimicking the Rieske oxygenases [69]. Whereas propyl 3,3,-bis(1-methylimidazol-2-yl)-propionate favored epoxidation (Table 2, entry 5), novel (di-(2-pyridyl)methyl) benzamide ligands showed predominantly formation of the *cis*-diol product in the oxidation of cyclooctene. This member of the N,N,O-ligand family was introduced by Que and coworkers in 2005 [70]. The iron(II) complexes of this ligand catalyzed the dihydroxylation of various aliphatic and aromatic olefines (Table 2, entry 6). It should be noted that the *cis*-diol to epoxide ratio is significantly increased and mainly the *cis*-diol is formed.

In 2008, Que and coworkers reported an asymmetric version of the dihydroxylation with a new type of ligands bearing bipyrrolidine as the chiral backbone [71]. The corresponding iron(II) complex showed general activity in the dihydroxylation of various olefins using H_2O_2. Satisfactory results are obtained with aliphatic as well as with aromatic olefins. For example, dihydroxylation of styrene gave styrene oxide and 1-phenylethane-1,2-diol in $<1\%$ and 65% yield, respectively (Scheme 10).



Scheme 10 Asymmetric epoxidation of *trans*-2-heptene with the chiral iron complex and H_2O_2

Most striking result goes to the oxidation of 2-heptene. In this system, the *cis*-diol is obtained in 55% yield with 97% *ee* (Scheme 10).[1] However, due to the unusual reaction conditions (large excess of olefin), this method is unlikely to be applied in organic synthesis. In-between homogeneous and heterogeneous iron catalysts, unsupported "free" nano-γ-Fe_2O_3 displays a unique opportunity to combine reusability with activity and selectivity. The nano-γ-Fe_2O_3 catalyst with a particle size of 20–50 nm showed oxidative cleavage of aromatic olefins to the corresponding aldehydes applying hydrogen peroxide as oxidant (Scheme 11) [72, 73]. Various aromatic olefins with different substituents were successfully oxidized into aldehydes with high selectivity although only low conversion was achieved. Interestingly, the catalytic activity can be tuned by changing the particle size of nano-iron oxide.



Scheme 11 Selective cleavage of olefins to aldehydes

4 Alkane Oxidation

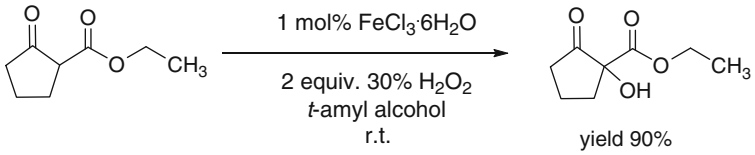
Saturated hydrocarbons are the main constituents of petroleum and natural gas. Mainly used as fuels for energy production they also provide a favorable, inexpensive feedstock for chemical industry [74]. Unfortunately, the inertness of alkanes renders their chemical conversion challenging with respect to selectivity. Clearly, the development of new and improved methods for the selective transformation of alkanes belongs to the central goals of catalysis. Iron-catalyzed processes might be a smart tool for such transformations (for reviews see [75–77]).

Remarkably, alkanes are oxidatively transformed by biological organisms at benign temperatures and pressures. Clearly, enzymatic transformations of alkanes and their well studied mechanisms (e.g., for cytochrome P450) are beyond the

[1]Yield and catalyst concentration based on the limiting reagent.

scope of the present review and the interested reader is referred to recent literature (for heme systems like Cytochrome P450 and for nonheme systems see [78–80]). However, as discussed in the previous section, these enzymes are inspiration for a broad range of heme and nonheme biomimetic model catalysts [81]. In addition, radical reactions based on Fenton chemistry offer possibilities for the oxidation of alkanes (for an overview about iron-catalyzed oxidation reactions see [82]).

A ligand-free oxidation of activated methylenes was reported by Bolm and coworkers with $Fe(ClO_4)_2$ as catalyst [83] and later with an $FeCl_3{\cdot}6H_2O$ as catalyst source in an improved system [84]. In the latter system, no acid was needed under $GoAgg^V$-type conditions, where pyridine was used as solvent. Benzylic oxidation was achieved to the corresponding carbonyl compounds (up to >99% yield) with aqueous TBHP (=*t*-butyl hydroperoxide) as terminal oxidant. Besides, alcohols are converted to the corresponding ketones. In 2008, we introduced an $FeCl_3{\cdot}6H_2O$ ligand-free catalyst system for the α-oxidation of β-ketoesters (Scheme 12) [85]. By using cyclic β-ketoesters as starting material 75–90% yield of the hydroxylation products are obtained with H_2O_2 as oxidant.

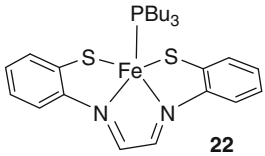


Scheme 12 Selective hydroxylation of 2-ethoxycarbonyl-1-oxo-cyclopentane

Inspired by $Gif^{III,IV}$ or $GoAgg^{III}$ type chemistry [77], iron carboxylates were investigated for the oxidation of cyclohexane, recently. For example, Schmid and coworkers showed that a hexanuclear iron *p*-nitrobenzoate $[Fe_6O_3(OH)(p\text{-}NO_2C_6H_4COO)_{11}(dmf)_4]$ with an unprecedented $[Fe_6^{III}O_3(\mu_3\text{-}O)(\mu_2\text{-}OH)]^{11+}$ core is the most active catalyst [86]. In the oxidation of cyclohexane with only 0.3 mol% of the hexanuclear iron complex, total yields up to 30% of the corresponding alcohol and ketone were achieved with 50% H_2O_2 (5.5–8 equiv.) as terminal oxidant. The ratio of the obtained products was between 1:1 and 1:1.5 and suggests a Haber–Weiss radical chain mechanism [87, 88] or a cyclohexyl hydroperoxide as primary oxidation product.

In contrary to the not easy adjustable ligand-free systems, systems with ligands provide possibilities in tuning activity and selectivity. Shul'pin et al. examined the addition of bipyridine to $FeCl_3$ and hydrogen peroxide as oxidant [89]. They monitored a 35 times enhanced reactivity (TON up to 400) for oxidation of cyclohexane. They observed the predominant formation of cyclohexyl hydroperoxide and the corresponding transformations into cyclohexanol and cyclohexanone. Another radical-based system involving cyclohexyl hydroperoxide was developed by Pombeiro and coworkers. They used an FeN_2S_2 center bearing a noninnocent ligand (Scheme 13) [90]. In the presence of pyrazinecarboxylic acid (Hpca) at room temperature within 6 h, yields up to 13% are achieved (alcohol as the major product).

Scheme 13 The FeN_2S_2 center bearing a coordinatively unsaturated iron(III) with a noninnocent ligand



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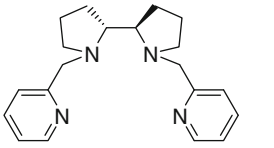
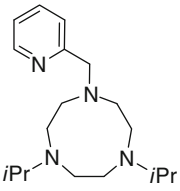
Based on Shul'pin's examinations on the rate enhancement by adding Hpca [91] and in contrast to the inhibition while adding Hpca [110], Reedjik and coworkers investigated the role of Hpca with defined iron complexes [92]. In their studies, $[Fe(pca)_2(py)_2]\cdot py$ showed moderate activity with a maximum yield of 31% based on hydrogen peroxide.

A major challenge in the application of "biomimetic" or "bio-inspired" ligands is to direct the unselective radical pathways of simple Fe salts and H_2O_2 into chemo-, regio-, and stereoselective transformations. Thus, homolytic cleavage of the iron peroxo bond has to be omitted. For this purpose, various N- and N,O-ligands were developed (for a review about "Biologically inspired oxidation catalysis" see [93]). Tridentate ligands like bis(imino)pyridine or bis(amino)pyridine turned out to be not appropriate. Here, two ligands can cover all coordination sites and the Fe complexes showed only moderate oxidation reactivity [94, 95]. More suitable ligands are those of tetradentate nitrogen-donor ligands. An arrangement that allows two *cis*-oriented coordination sites for peroxide binding is also necessary as stated by Que [96]. During the past decade, tetradentate N_4-ligands and recently N,O-ligands showed interesting activity not only in olefin oxidation but also in more challenging alkane oxidation. Scheme 14 shows important N-ligands, which have been used in such reactions.



PDP **23** R = H, Me



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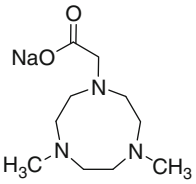
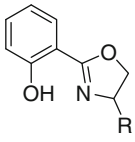
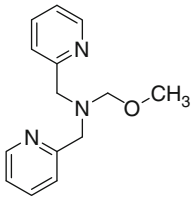


TACN **25**

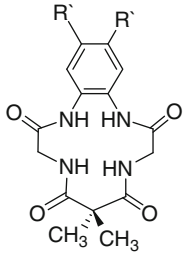


Hphox

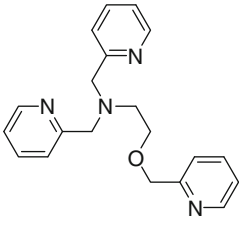
26 R = COOH, *i*Pr



mebpa **27**



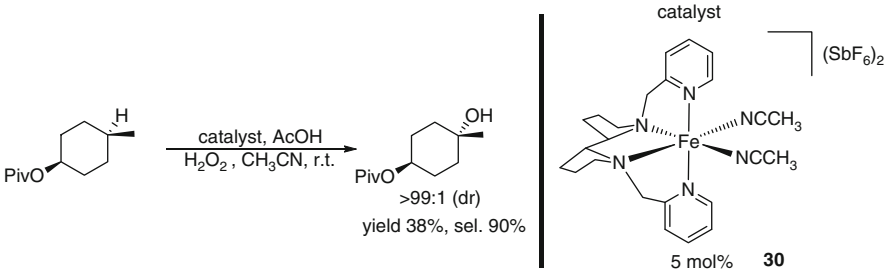
TAML **28** CH_3 = alkyl; R` = H, OMe, Cl



tpoen **29**

Scheme 14 Biomimetic ligands used in iron-catalyzed alkane oxidation

The first example of a nonheme iron catalyst with the TPA ligand **2**, which effected stereospecific alkane hydroxylation, was developed by Que and coworkers in 1997 [97]. In the same year, the linear N_4 tetradentate mep or BPMEN **1** ligand was reported by Nishida and coworkers [98]. [Fe(**1**)$(OTf)_2$] complexes are characterized by two essential pyridine donors connected with an ethylendiamine bridge, two labile *cis*-coordination sites at the metal center and single *cis-a* coordination geometry [99]. Therefore, iron complexes of **1** are quite stable against the addition of excessive H_2O_2 (up to 100 equiv. excess) and show a reactivity that is distinct from Fenton-type chemistry. Hence, the catalyst converts 65% of the H_2O_2 into oxygenated products using 10 equiv. of H_2O_2 [100]. A breakthrough in selective alkane oxidation was reported in 2007 by Chen and White, who developed a catalyst system based on a modified mep ligand. The resulting hydroxylation catalyst [Fe(*S*,*S*-**30**)$(CH_3CN)_2$]$(SbF_6)_2$ reacts with electron-rich, tertiary C–H bonds using H_2O_2 in good yields with predictable selectivity (Scheme 15) [101].

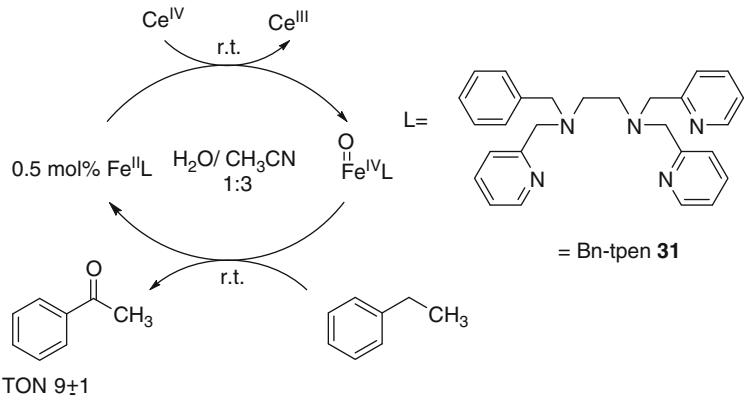


Scheme 15 Selective C–H hydroxylation by Chen and White

The addition of acetic acid (0.5 equiv. to the substrate) to the catalyst system led to increased activity (doubling of yield) by maintaining the selectivity with 1.2 equiv. H_2O_2 as terminal oxidant. Advantageously, the system is characterized by a certain tolerance towards functional groups such as amides, esters, ethers, and carbonates. An improvement in conversions and selectivities by a slow addition protocol was shown recently [102]. For the first time, a nonheme iron catalyst system is able to oxidize tertiary C–H bonds in a synthetic applicable and selective manner and therefore should allow for synthetic applications [103].

Recently, Nam, Fukuzumi, and coworkers succeed in an iron-catalyzed oxidation of alkanes using Ce(IV) and water. Here, the generation of the reactive nonheme iron (IV) oxo complex is proposed, which subsequently oxidized the respective alkane (Scheme 16) [104]. With the corresponding iron(II) complex of the pentadentate ligand **31**, it was possible to achieve oxidation of ethylbenzene to acetophenone (9 TON). ^{18}O labeling studies indicated that water is the oxygen source.

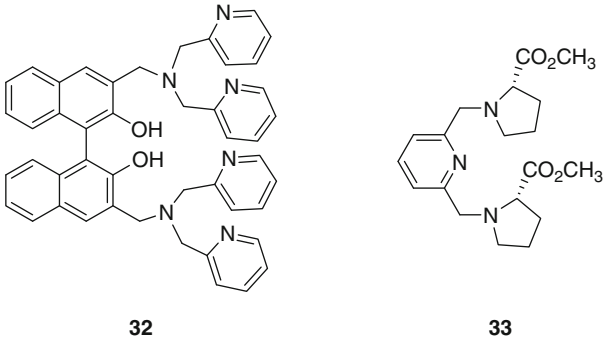
In addition to tri- [105] and tetradentate N-ligands, mononuclear and dinuclear iron complexes with pentadentate N,N,N,N,O-ligands were applied to alkane



Scheme 16 Oxidation of ethylbenzene with Ce(IV)

oxidations. As an example Sun and Wang used tpoen, **29** in the oxidation of cyclohexane [106]. Mediocre conversion (18%) based on the oxidant H_2O_2 are observed. Another multidentate ligand (mebpa, **27**) was reported by Reedjik (first report on the mebpa ligand: [107, 108]). At low H_2O_2 concentration in the presence of additives, they succeeded in 54% conversion with an alcohol/ketone ratio up to 3.5.

A mononuclear diastereopure high-spin Fe^{III} alkylperoxo complex with a pentadentate N,N,N,O,O-ligand **33** (Scheme 17) was reported by Klein Gebbink and coworkers [109, 110]. The complex is characterized by unusual seven-coordinate geometry. However, in the oxidation of ethylbenzene the iron complex with **33** and TBHP yielded with large excess of substrate only low TON's (4) and low ee (6.5%) of 1-phenylethanol.

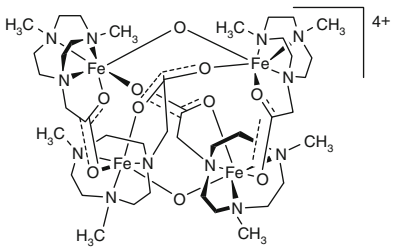


32 **33**

Scheme 17 Biomimetic ligands used in Fe-catalyzed alkane oxidations

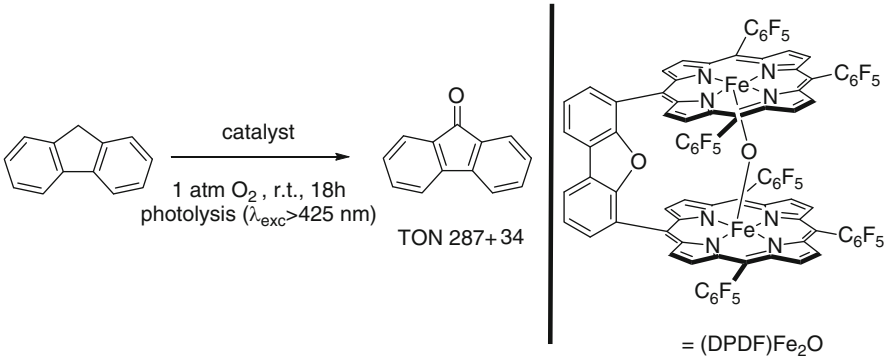
For nearly two decades TACN-type ligands are of continuing interest for oxidation chemistry. A more recent example is described by Shul'pin and coworkers, who prepared novel di- and tetranuclear complexes with TACN ligands **25** bearing pendant acetato arms bridging the iron(III) centers (Scheme 18) [111]. The

Scheme 18 Tetranuclear $[Fe_4(N_3O_2\text{-}L_4(\mu\text{-}O)_2)]^{4+}$ complex with 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane (**25**) ligands



tetranuclear catalyst showed improved productivity (TON = 43) in cyclohexane oxidation with H_2O_2 as oxidant with an alcohol/ketone (A/K) ratio of 6. Similarities in the A/K ratio conclude a radical pathway, e.g., Fenton chemistry, for this reaction.

Apart from selective organic synthesis, there exists a significant interest in the nonselective iron-catalyzed oxidations of all kinds of organic compounds. In this respect, Collins and coworkers developed and examined tetraamido macrocyclic ligands (TAML, **28**) for the treatment of waste water from paper and textile mills with H_2O_2 [112]. During their investigations, Fe(V)-oxo species and Fe(IV) complexes were proposed and observed as key intermediates [113]. Notably, the isolated Fe (V)-oxo species gave substoichiometric reactions with olefins and with ethylbenzene [4]. For hydrocarbon decompositions also photocatalytic oxidations were reported in 2006 by Nocera and coworkers. More specifically, they used fluorinated Pacman bisporphyrin ligands bridged by a dibenzofuran scaffold with visible light and oxygen as terminal oxidant (Scheme 19) [114].

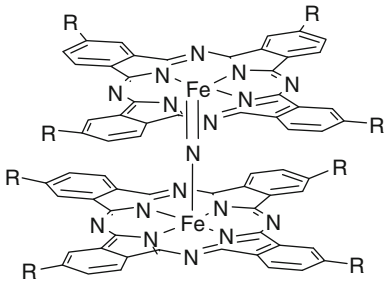


Scheme 19 Photocatalytic hydroxylation of fluorene with a Pacman system

The Pacman catalyst selectively oxidized a broad range of organic substrates including sulfides to the corresponding sulfoxides and olefins to epoxides and ketones. However, cyclohexene gave a typical autoxidation product distribution yielding the allylic oxidation products 2-cyclohexene-1-ol (12%) and 2-cyclohexene-1-one (73%) and the epoxide with 15% yield [115].

In addition to porphyrin-type ligands, also porphyrazine complexes show interesting properties such as activation of H_2O_2 and pH-dependent decomposition of dyes [116]. Recently, Sorokin and coworkers applied binuclear phthalocyanine complexes for the oxidation of methane [117]. With their μ-nitrido-bridged phthalocyanine complexes (Scheme 20), they were able to perform homogenous oxidation in CH_3CN to give formic acid with H_2O_2 as oxidant.

Scheme 20 μ-Nitrido-bridged iron phthalocyanine complexes



34 R = H, $C(CH_3)_3$

Labeling studies indicated that the obtained formic acid was originated from both substrate and solvent. When the catalyst was supported onto silica to provide a heterogeneous catalyst, methane is oxidized at 80 °C and 32 bars CH_4 to CH_2O (up to 1.1 TON) and HCOOH (up to 27.3 TON).

Metal-oxygen cluster species such as polyoxometalates (POM's) represent an interesting and interdisciplinary field in oxidation catalysis. Especially, high-valent iron–oxo species of POM's should be highly active catalysts [118]. Unfortunately, until today experimental investigations did not prove the existence of this type of powerful oxidants. Novel protocols for the oxidation of alkanes with Fe-containing POM's include the use of iron-supported polyoxotungstates ($FeSiW_{11}$) for the oxidation of cyclohexane in the presence of microwave-induced heating [119, 120]. More specifically, tetrairon(III)-substituted polytungstates immobilized on (3-aminopropyl)triethoxysilane (apts)-modified SBA-15 showed high catalytic activity in the oxidation of long chain alkanes [121]. For example, *n*-hexadecane gave 18% conversion (TOF = 2,043 h^{-1}) using air as oxidant at 150 °C. Selectivities of 50% C_{16} ketones and 28% C_{16} alcohols were obtained. Mechanistic investigations showed that the reaction occurred via a free-radical chain autooxidation.

5 Oxidation of Aromatic C–H Bonds

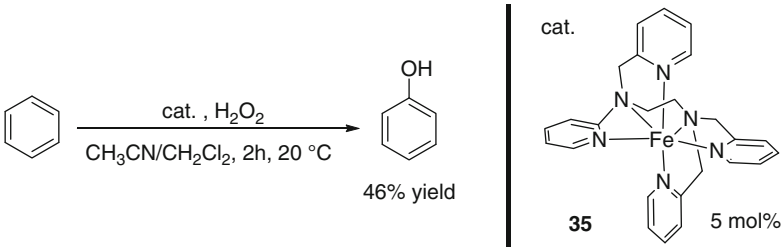
Selective C–H hydroxylation on arenes to give the corresponding phenols displays an attractive tool for the chemical industry and organic synthesis. Unfortunately, the desired phenolic product is more electron rich than the substrate and therefore

tends to over-oxidation resulting in catechols, hydroquinones, benzoquinones, and finally tars.

Already in the beginning of the nineteenth century, radical reactions on arenes with iron(II)sulfate and H_2O_2 were discovered, known as Fenton reaction. Later on, numerous attempts were undertaken to direct the unselective radical reactions to more selective ones by employing different oxidants, ligands, biphasic systems, photochemistry, or electro-catalytic methods. More recent examples include the work of Bianchi et al. who reported enhanced selectivity for benzene oxidation by the addition of a pyrazine-carboxylate ligand under biphasic conditions [122]. At a conversion of 8.6%, 85% selectivity based on H_2O_2 and 97% selectivity based on benzene were observed. Pombeiro and coworkers improved the conversion and selectivity by using Fe^{III}(gma)(PBu_3) as catalyst, which was also active in alkane oxidation [90]. The oxidation of benzene proceeded under rather mild reaction conditions (r.t., 6 h) and yielded 20% (110 TON) phenol without any other observed by-products and hydrogen peroxide as terminal oxidant (4 equiv. with respect to benzene). Another biphasic approach made use of iron(II)sulfate as catalyst and H_2O_2 as oxidant in a system with a polypropylene hydrophobic porous support as separation barrier [123]. The performance in terms of conversion is low (up to 1.2%). Not surprisingly, the selectivities to corresponding phenol (99.9%) and H_2O_2 conversions to phenol (96.8%) were excellent. It is well-known from heterogeneous catalyst systems that at higher conversion the selectivities will be lower. A micro-emulsion catalytic system consisting of water, benzene, acetic acid, ferric dodecane sulfonate as catalyst and sodium dodecylbenzene sulfonate as surfactant was shown to be also applicable for hydroxylation of benzene with H_2O_2 as oxidant [124]. With low H_2O_2/benzene ratio phenol selectivities up to 92.9% could be achieved, at 21.9% benzene conversion. At higher H_2O_2 concentration, benzene conversion is enhanced but with the disadvantage of a more unselective reactions.

In the field of nonheme aromatic hydroxylations the oxidation of benzoic acids to salicylic acid was investigated. In 2005, the group of Rykbak-Akimova achieved stoichiometric hydroxylation of benzoic acid with an $[Fe^{II}(\mathbf{1})(CH_3CN)_2](ClO_4)_2$ complex and H_2O_2 as oxidant to yield exclusively *o*-hydroxylated salicylate complex $[Fe^{III}(\mathbf{1})(OOC(C_6H_4)O)](ClO_4)_3$ (up to 84% at r.t.) [125]. In the same year, Nam and coworkers reported that perbenzoic acid is converted into salicylate complexes while reacting with $[Fe^{II}(\mathbf{2})(CH_3CN)_2]^{2+}$ [126]. Several investigations were performed with nonheme iron(II)complexes of Bn-tpen **31** and N_4Py. They resulted in the conclusion that the iron(IV)-oxo group attacks the aromatic ring via an electrophilic pathway to produce either a tetrahedral radical or cationic σ-complex [127]. A catalytic transformation of arenes was achieved with nonheme iron complexes of tpen ligands **35** (Scheme 21) [128]. Addition of a reducing agent (1-naphthol) enhanced in most cases the yields of substrates; e.g., 59% yield of phenol.[2]

[2]Yields are based on the limiting reagent.

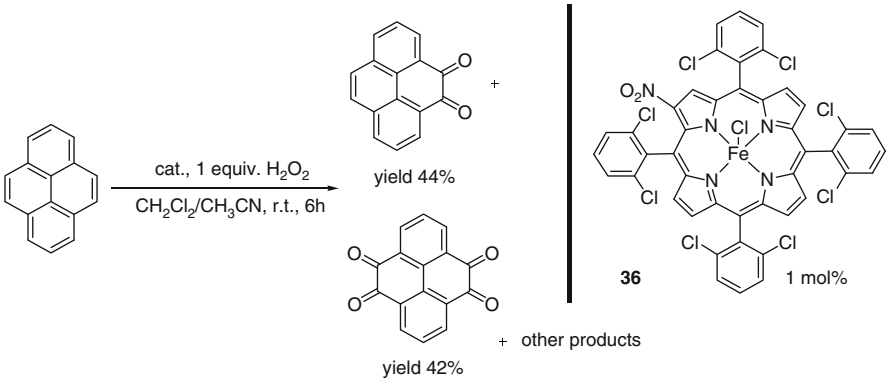


Scheme 21 Hydroxylation of benzene to phenol with nonheme iron complex **35** [142]

In addition to nonheme iron complexes also heme systems are able to catalyze the oxidation of benzene. For example, porphyrin-like phthalocyanine structures were employed to benzene oxidation (see also alkane hydroxylation) [129]. Mechanistic investigations of this type of reactions were carried out amongst others by Nam and coworkers resulting in similar conclusions like in the nonheme case [130]. More recently, Sorokin reported a remarkable "biological" aromatic oxidation, which occurred via formation of benzene oxide and involves an NIH shift. Here, phenol is obtained with a TON of 11 at r.t. with 0.24 mol% of the catalyst.

Compared with the selective hydroxylation of arenes or polyarenes to phenols, similar reactions to quinones were so far of limited interest. Again, the stability of the corresponding products under the reaction conditions is often problematic. Nevertheless, this type of reaction is of industrial interest for the preparation of vitamin intermediates. Here, menadione (vitamin K_3) and 2,3,6-trimethylquinone (key intermediate in vitamin E synthesis) represent the most important intermediates. Moreover, polynuclear partly functionalized aromatic hydrocarbons (PAHs) are a central class of environmental carcinogens and the complete oxidation and decomposition is important for environmentally benign waste disposals (mostly wet air oxidations are used for decomposition of PAH's; for iron-catalyzed examples see [131, 132]). For the oxidation of such compounds, metalloporphyrins are applied as models for cytochrome P450. Thus, 1 mol% *o*-substituted tetraarylporphyrinatoiron(III)chloride with electron withdrawing groups at the porphyrin ring as well as at the phenyl rings gave with H_2O_2 as oxidant high conversion for different PAH's. For example, the oxidation of pyrene proceeded in up to 92% conversion and resulted in two major products (pyrene-4,5-dione, pyrene-4,5,9,10-tetrone) (Scheme 22) [133].

Previous studies by Sorokin with iron phthalocyanine catalysts made use of oxone in the oxidation of 2,3,6-trimethylphenol [134]. Here, 4 equiv. $KHSO_5$ were necessary to achieve full conversion. Otherwise, a hexamethyl-biphenol is observed as minor side-product. Covalently supported iron phthalocyanine complexes also showed activity in the oxidation of phenols bearing functional groups (alcohols, double bonds, benzylic, and allylic positions) [135]. Besides, silica-supported iron phthalocyanine catalysts were reported in the synthesis of menadione [136].



Scheme 22 Oxidation of pyrene with Fe-porphyrin catalysts

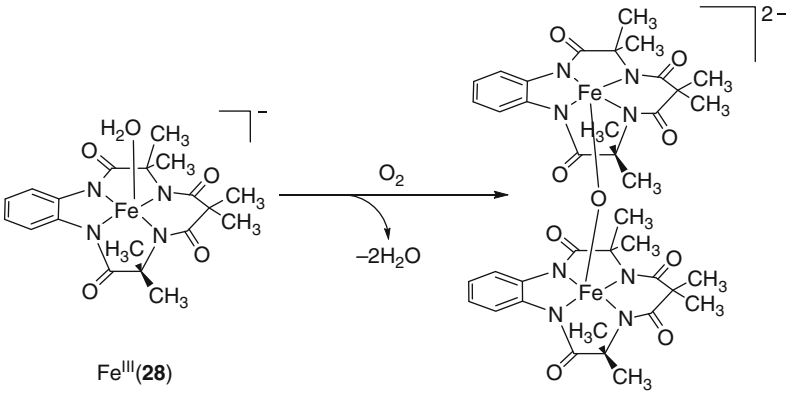
6 Alcohol Oxidations

A number of easily available iron salts and complexes can be used for the selective oxidation of alcohols to carbonyl compounds. Often iron oxo species are proposed as catalytic intermediates. Examples include the simple combination of $FeCl_3$ and hydrogen peroxide, which is known to be of moderate activity in alcohol oxidations as shown in the case of 2-cyanoethanol [137]. An $FeCl_3$–TEMPO–$NaNO_2$ catalyst system using air as oxidant was introduced in 2005 [138]. At ambient temperature various alcohols including sulfur-containing compounds were converted to the corresponding aldehydes and ketones with high conversion and excellent selectivities. Pearson and coworkers presented an iron carbonyl precatalyst (1,3-cyclohexadiene) $Fe(CO)_3$ in the presence of triethylamine-*N*-oxide as oxidant yielding the corresponding carbonyl compounds in 88–98% yield [139].

Under solvent-free conditions in the presence of stoichiometric amounts of iron nitrate good to very good yields for the oxidation of benzyl and various secondary alcohols were obtained [140]. Despite these examples, controlling iron-catalyzed oxidation reactions of alcohols with air or hydrogen peroxide remain difficult. In 2008, we demonstrated the possibility to switch between nonselective radical pathways and selective nonradical reactions by tuning the absolute pH of the reaction system [141]. As a benchmark reaction, the oxidation of benzyl alcohol was studied, which is catalyzed by various iron salts (mainly $Fe(NO_3)_3$) to give benzaldehyde. A constant pH value resulted in high conversion (pH value close to 1.00), whereas the chemoselectivity is controlled by the change of the pH.

In the field of nonheme iron complexes, Münck, Collins, and Kinoshita reported the oxidation of benzylic alcohols via stable μ-oxo-bridged diiron(IV) TAML complexes, which are formed by the reaction of iron-**28** complexes with molecular oxygen (Scheme 23) [142].

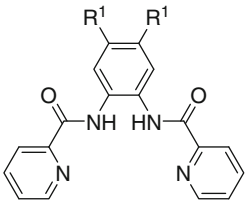
Remarkably, the shown Fe^{III} complexes reacted directly with oxygen to afford high-valent oxo–iron species. In addition, Kim, Nam, and coworkers explored



Scheme 23 Formation of the catalytic active μ-oxo-bridged diiron(IV) complex

mechanistic details of the alcohol oxidation with heme and nonheme complexes [143]. They suggested that this oxidation occurred via a α-CH hydrogen atom abstraction followed by an electron transfer. Later Kim and coworkers reported an iron(III) complex with tetradentate ligands bearing amide moieties (Scheme 24) [32]. These complexes oxidized alcohols as well as olefins to the corresponding carbonyls and epoxides on treatment with *m*CPBA as oxidant. However, low TON's between 50 and 90 were achieved using unusual substrate:oxidant:catalyst ratio of 100:10:0.5.

Scheme 24 Biomimetic ligands **37** and **38**



37: $R^1 = CH_3$
38: $R^1 = Cl$

A biomimetic oxidation with perfluorinated porphyrin complexes [(F_{20}TPP) FeCl] showed high catalytic activity with secondary alcohols with over 97% yield in all cases [144]. Furthermore, this catalyst is able to oxidize a broad range of alcohols under mild conditions with *m*CPBA as terminal oxidant. Here, an α-hydroxyalkyl radical species is proposed as central intermediate.

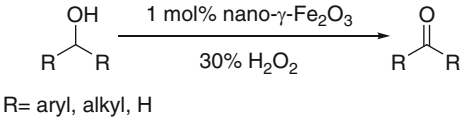
Another iron porphyrin complex with 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrin was applied in ionic liquids and oxidized veratryl alcohol (3,4-dimethoxybenzyl alcohol) with hydrogen peroxide in yields up to 83% to the aldehyde as the major product [145]. In addition, TEMPO was incorporated via

a phenyl linker into the porphyrin scaffold [146]. The resulting catalyst showed a slight increase of the activity in the oxidation of benzyl alcohol using bleach as oxidant. However, similar Mn-based complexes showed distinct better activity.

Finally, phthalocyanine iron catalysts were also used for the oxidation of alcohols to yield corresponding carbonyl compounds with nonbenign hypervalent iodine oxidants [147].

Interestingly, "free" nano-iron oxide particles are active catalysts for the selective oxidation of alcohols to yield the corresponding aldehydes/ketones [72, 73]. Different aromatic alcohols and secondary aliphatic alcohols were oxidized with high selectivity, but at low conversion. Here, further improvement should be possible (Scheme 25).

Scheme 25 Selective oxidation of alcohols to aldehydes and ketones



Under microwave irradiation and applying MCM-41-immobilized nano-iron oxide higher activity is observed [148]. In this case also, primary aliphatic alcohols could be oxidized. The TON for the selective oxidation of 1-octanol to 1-octanal reached to 46 with 99% selectivity. Hou and coworkers reported in 2006 an iron coordination polymer $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ with fcz = 1-(2,4-difluorophenyl)-1,1-bis[(1*H*-1,2,4-triazol-l-yl)methyl]ethanol which catalyzed the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as oxidant in 87% yield and up to 100% selectivity [149]. An alternative approach is based on the use of heteropoly acids, whereby the incorporation of vanadium and iron into a molybdophosphoric acid catalyst led to high yields for the oxidation of various alcohols (up to 94%) with molecular oxygen [150].

7 Conclusions

Iron-based redox reactions are of key importance for the correct function of biological systems. Often in these systems, high-valent iron–oxo species are proposed as crucial intermediates. In the past decade, significant advancements have been reported with respect to the understanding and characterization of such active iron oxo species. However, despite all this work still the development of synthetically useful iron catalysts is significantly driven by the synthesis of new ligands and catalytic testing. Notably, selective catalytic oxidations with iron complexes allow to "streamline" organic synthesis and to perform the synthesis of advanced intermediates with improved efficiency.

References

1. Sheldon RA (1994) Metalloporphyrins in catalytic oxidations. Marcel Dekker, New York
2. Trautheim AX (1997) Bioinorganic chemistry: transition metals in biology and their coordination chemistry. Wiley-VCH, Weinheim
3. Berry JF, Bill E, Bothe E, George SD, Miener B, Neese F, Wieghardt K (2006) Science 312:1937–1941
4. Bukowski MR, Koehntop KD, Stubna A, Bominaar EL, Halfen JA, Munck E, Nam W, Que L (2005) Science 310:1000–1002
5. de Oliveira FT, Chanda A, Banerjee D, Shan X, Mondal S, Que L, Bominaar EL, Münck E, Collins TJ (2007) Science 315:835–838
6. Krebs C, Fujimori DG, Walsh CT, Bollinger JM (2007) Acc Chem Res 40:484–492
7. Makris TM, von Koenig K, Schlichting I, Sligar SG (2006) J Inorg Biochem 100:507–518
8. Yudin AK (2006) Aziridines and epoxides in organic synthesis. Wiley-VCH, Weinheim, pp 229–269
9. Larrow JF, Jacobsen EN (2004) Topics Organomet Chem 6:123–152
10. Jacobsen EN, Pfaltz A, Yamamoto H (1999) Comprehensive asymmetric catalysis, vol 3., pp 1309–1326
11. Plietker B (2008) Iron catalysis in organic chemistry. Wiley-VCH, Weinheim, pp 73–123
12. Enthaler S, Junge K, Beller M (2008) Angew Chem 120:3363–3367, Angew Chem Int Ed 47:3317–3321
13. Bäckvall J-E (2004) Modern oxidation methods. Wiley-VCH, Weinheim, pp 22–50
14. Punniyamurthy T, Velusamy S, Iqbal J (2005) Chem Rev 105:2329–2363
15. Simándi LI (2003) Advances in catalytic activation of dioxygen by metal complexes. Kluwer, Dordrecht
16. Souza DPB, Fricks AT, Alvarez HM, Salomão GC, Olsen MHN, Filho LC, Fernandes C, Atunes OAC (2007) Catal Commun 8:1041–1046
17. Traylor TG, Tsuchiya S, Byun YS, Kim C (1993) J Am Chem Soc 115:775–2781
18. Stephenson NA, Bell AT (2007) J Mol Catal A Chem 275:54–62
19. Stephenson NA, Bell AT (2005) J Am Chem Soc 127:8635–8643
20. Bassan A, Blomberg MRA, Siegbahn PEM, Que L (2005) Angew Chem 117:2999–3001, Angew Chem Int Ed 44:2939–2941
21. Kodera M, Itoh M, Kano K, Funabiki T, Reglier M (2005) Angew Chem 117:7266–7268, Angew Chem Int Ed 44:7104–7106
22. Fujita M, Que L (2004) Adv Synth Catal 346:190–194
23. Chen K, Costas M, Kim J, Tipton AT, Que L (2002) J Am Chem Soc 124:3026–3035
24. White MC, Doyle AG, Jacobsen EN (2001) J Am Chem Soc 123:7194–7195
25. Costas M, Tipton AK, Chen K, Jo D-H, Que L (2001) J Am Chem Soc 123:6722–6723
26. Chen K, Que L (1999) Chem Commun 1375–1376
27. Mas-Ballesté R, Que L (2007) J Am Chem Soc 129:15964–15972
28. Mas-Ballesté R, Costas M, Van den Berg T, Que L (2006) Chem Eur J 12:7489–7500
29. Bukowski MR, Comba P, Lienke A, Limberg C, De Laorden CL, Mas-Ballesté R, Merz M, Que L (2006) Angew Chem 118:3524–3528, Angew Chem Int Ed 45:3446–3449
30. Duban E A, Bryliakov K P, Talsi E P (2007) Eur J Inorg Chem 852–857
31. Bautz J, Comba P, De Laorden CL, Menzel M, Rajaraman G (2007) Angew Chem 119:8213–8216, Angew Chem Int Ed 46:8067–8070
32. Lee SH, Han JH, Kwak H, Lee SJ, Lee EY, Kim HJ, Lee JH, Bae C, Lee CN, Kim Y, Kim C (2007) Chem Eur J 13:9393–9398
33. Suh Y, Seo MS, Kim KM, Kim YS, Jang HG, Tosha T, Kitagawa T, Kim J, Nam W (2006) J Inorg Biochem 100:627–633
34. Gosiewska S, Lutz M, Spek AL, Klein Gebbink RJM (2007) Inorg Chim Acta 360:405–417
35. Taktak S, Ye W, Herrera AM, Rybak-Akimova EV (2007) Inorg Chem 46:2929–2942
36. Liu P, Wong EL-M, Yuen AW-H, Che C-M (2008) Org Lett 10:3275–3278

37. Bitterlich B, Schröder K, Tse MK, Beller M (2008) Eur J Org Chem 29:4867–4870
38. Bitterlich B, Anilkumar G, Gelalcha FG, Spilker B, Grotevendt A, Jackstell R, Tse MK, Beller M (2007) Chem Asian J 2:521–529
39. Gopinathan A, Bitterlich B, Gelalcha FG, Tse MK, Beller M (2007) Chem Commun 289–291
40. Schröder K, Enthaler S, Bitterlich B, Schulz T, Spannenberg A, Tse MK, Junge K, Beller M (2009) Chem Eur J 15:5471–5481
41. Schröder K, Tong X, Bitterlich B, Tse MK, Gelalcha FG, Brückner A, Beller M (2007) Tetrahedron Lett 48:6339–6342
42. Costas M, Tipton AK, Chen K, Jo D-H, Que L (2001) J Am Chem Soc 123:6722–6723
43. Francis MB, Jacobsen EN (1999) Angew Chem Int Ed 38:937–941
44. Cheng QF, Xu XY, Ma WX, Yang SJ, You TP (2005) Chin Chem Lett 16:1467–1470
45. Gelalcha FG, Anilkumar G, Tse MK, Brückner A, Beller M (2008) Chem Eur J 14:7687–7698
46. Gelalcha FG, Bitterlich B, Gopinathan A, Tse MK, Beller M (2007) Angew Chem 119:1–6, Angew Chem Int Ed 46:1–5
47. Marchi-Delapierre C, Jorge-Robin A, Thibon A, Ménage S (2007) Chem Commun 1166–1168
48. Yeung H-L, Sham K-C, Tsang C-S, Lau T-C, Kwong H-L (2008) Chem Commun 3801–3803
49. Rose E, Andrioletti B, Zrig S, Quelquejeu-Ethève M (2005) Chem Soc Rev 34:573–583
50. Gupta KC, Sutar AK (2008) Polym Adv Technol 19:186–200
51. Gupta KC, Sutar AK (2008) J Appl Polym Sci 108:3927–3941
52. Wang Y, Zhang Q, Shishido T, Takehira K (2002) J Catal 209:186–196
53. Nozaki C, Lugmair CG, Bell AT, Tilley TD (2002) J Am Chem Soc 124:13194–13203
54. Duma V, Hönicke D (2000) J Catal 191:93–104
55. Terry TJ, Dubois G, Murphy A, Stack TD (2007) Angew Chem 119:963–965, Angew Chem Int Ed 46:945–947
56. Dubois G, Murphy A, Stack TD (2003) Org Lett 5:2469–2472
57. Salavati-Niasari M (2007) J Mol Catal 278:22–28
58. Weissermehl K, Arpe H J (2003) Worldwide production capacities for ethylene glycol in 2000: 13.6 Mio to/a; worldwide production of 1,2-propylene glycol in 1996: 1.4 Mio to/a. In: Ind Org Chem, Vol 4. Wiley-VCH, Weinheim, p 152 and p 277
59. Zaitsev AB, Adolfsson H (2006) Synthesis 1725–1756
60. Costas M, Mehn MP, Jensen MP, Que L (2004) Chem Rev 104:939–986
61. Oldenburg PD, Que L (2006) Catal Today 117:15–21
62. Bruijnincx PCA, Van Koten G, Klein Gebbink RJM (2008) Chem Soc Rev 37:2716–2744
63. Feng Y, Ke C-Y, Xue G, Que L (2009) Chem Commun 50–52
64. Company A, Gómez L, Fontrodona X, Ribas X, Costas M (2008) Chem Eur J 14:5727–5731
65. Company A, Feng Y, Güell M, Ribas X, Luis JM, Que L, Costas M (2009) Chem Eur J 15:3359–3362
66. Koehntop KD, Emerson JP, Que L (2005) J Biol Inorg Chem 10:87–93
67. Bruijnincx PCA, Lutz M, Spek AL, Van Faasen EL, Weckhuysen BM, Van Koten G, Klein Gebbink RJM (2005) Eur J Inorg Chem 779–787
68. Bruijnincx PCA, Lutz M, Spek AL, Hagen WR, Weckhuysen BM, Van Koten G, Klein Gebbink RJM (2007) J Am Chem Soc 129:2275–2286
69. Bruijnincx PCA, Buurmans ILC, Gosiewska S, Moelands MAH, Lutz M, Spek AL, Van Koten G, Klein Gebbink RJM (2008) Chem Eur J 14:1228–1237
70. Oldenburg PD, Shteinman AA, Que L (2005) J Am Chem Soc 127:15672–15673
71. Suzuki K, Oldenburg PD, Que L (2008) Angew Chem 120:1913–1915, Angew Chem Int Ed 47:1887–1889
72. Shi F, Tse MK, Pohl M-M, Brückner A, Zhang S, Beller M (2007) Angew Chem Int Ed 46:8866–8868

73. Shi F, Tse MK, Pohl M-M, Radnik J, Brückner A, Zhang S, Beller M (2008) J Mol Catal 292:28–35
74. Brazdil JF (2006) Top Catal 38:289–294
75. Bauer EB (2008) Current Org Chem 12:1341–1369
76. Shilov AE, Shul'pin GB (1997) Chem Rev 97:2879–2932
77. Labinger JA, Bercaw JE (2002) Nature 417:507–514
78. Ortiz de Montellano PR (2005) Cytochrome P450: structure, mechanism and biochemistry, 3rd edn. Kluwer/Plenum, New York
79. Abu-Omar MM, Loaiza A, Hontzeas N (2005) Chem Rev 105:2227–2252
80. Chakrabarty S, Austin RN, Deng D, Groves JT, Lipscomb JD (2007) J Am Chem Soc 129:3514–3515
81. Meunier B (2000) Biomimetic oxidation catalyzed by transition metal complexes. College Press, London
82. Plietker B (2008) Iron catalysis in organic chemistry. Wiley-VCH, Weinheim, pp 73–91
83. Pavan C, Legros J, Bolm C (2005) Adv Synth Catal 347:703–705
84. Nakanishi M, Bolm C (2007) Adv Synth Catal 349:861–864
85. Li D, Schröder K, Bitterlich B, Tse MK, Beller M (2008) Tetrahedron Lett 49:5976–5979
86. Trettenhahn G, Nagl M, Neuwirth N, Arion VB, Jary W, Pöchlauer P, Schmid W (2006) Angew Chem 118:2860–2865, Angew Chem Int Ed 45:2794–2798
87. Haber F, Willstätter R (1931) Ber Dtsch Chem Ges 64:2844–2856
88. Haber F, Weiss J (1932) Naturwissenschaften 20:948–950
89. Shul'pin GP, Golfeto CC, Süss-Fink G, Shul'pina LS, Mandelli D (2005) Tetrahedron Lett 46:4563–4567
90. Fernandes RR, Kirillova MV, da Silva JAL, Fraústo da Silva JJR, Pombeiro AJL (2009) Appl Catal A Gen 353:107–112
91. Shul'pin GP, Nizova GV, Kozlov YN, Cuervo LG, Süss-Fink G (2004) Adv Synth Catal 346:317–332
92. Tanase S, Marques-Gallego P, Browne WR, Hage R, Bouwman E, Feringa BL, Reedijk J (2008) Dalton Trans 2026–2033
93. Que L, Tolman WB (2008) Nature 455:333–340
94. Britovsek GJP, England J, Spitzmesser SK, White AJP, Williams DJ (2005) Dalton Trans 945–955
95. Carvalho NMF, Horn A, Antunes OAC (2006) Appl Catal A Gen 305:140–145
96. Oldenburg PD, Ke C-Y, Tipton AA, Shteinman AA, Que L (2006) Angew Chem 118:8143–8146, Angew Chem Int Ed 45:7975–7978
97. Kim C, Chen K, Kim J, Que L (1997) J Am Chem Soc 119:5964–5965
98. Okuno T, Ito S, Ohba S, Nishida Y (1997) J Chem Soc Dalton Trans 3547–3551
99. England J, Davies CR, Banaru M, White AJP, Britovsek GJP (2008) Adv Synth Catal 350:883–897
100. Britovsek GJP, England J, White AJP (2005) Inorg Chem 44:125–8134
101. Chen MS, White C (2007) Science 318:783–787
102. Vermeulen NA, Chen MS, White MC (2009) Tetrahedron 65:3078–3081
103. Christmann M (2008) Angew Chem 120:2780–2783, Angew Chem Int Ed 47:2740–2742
104. Lee Y-M, Dhuri SN, Sawant SC, Cho J, Kubo M, Ogura T, Fukuzumi S, Nam W (2009) Angew Chem 121:1835–1838, Angew Chem Int Ed 48:1803–1806
105. Godbole MD, Puig MP, Tanase S, Kooijman H, Spek AL, Bouwman E (2007) Inorg Chim Acta 360:1954–1960
106. Li F, Wang M, Ma C, Gao A, Chen H, Sun L (2006) Dalton Trans 2427–2434
107. Ito S, Okuno T, Itoh H, Ohba S, Matsushima H, Tokii T, Nishida Y (1997) Z Naturforsch B 52:719–727
108. Tanase S, Foltz C, De Gelder R, Hage R, Bouwman E, Reedijk J (2005) J Mol Catal A Chem 225:161–167

109. Gosiewska S, Cornlissen JLM, Lutz M, Spek AL, Van Knoten G, Klein Gebbink RJM (2006) Inorg Chem 45:4214–4227
110. Gosiewska S, Permentier HP, Bruins AP, Van Knoten G, Klein Gebbink RJM (2007) Dalton Trans 3365–3368
111. Romakh VB, Therrien B, Süss-Fink G, Shul'pin GB (2007) Inorg Chem 46:3166–3175
112. Collins TJ (2002) Acc Chem Res 35:782–790
113. Chanda A, Shan X, Chakrabarti M, Ellis WC, Popescu DL, Tiago de Oliveira F, Wang D, Que L, Collins TJ, Münck E, Bominaar EL (2008) Inorg Chem 47:3669–3678
114. Rosenthal J, Luckett TD, Hodgkiss JM, Nocera DG (2006) J Am Chem Soc 128:6546–6547
115. Rosenthal J, Pistorio BJ, Cheng LJ, Nocera DG (2005) J Org Chem 70:1885–1888
116. Theodoridis A, Maigut J, Puchta R, Kudrik EV, Van Eldik R (2008) Inorg Chem 47: 2994–3013
117. Sorokin AB, Kudrik EV, Bouchu D (2008) Chem Commun 2562–2564
118. Kumar D, Derat E, Khenkin AM, Neumann R, Shaik S (2005) J Am Chem Soc 127:17712–17718
119. Bonchio M, Carraro M, Scorrano G, Kortz U (2005) Adv Synth Catal 347:1909–1912
120. Bonchio M, Carraro M, Sartorel A, Scorrano G, Kortz U (2006) J Mol Catal A Chem 251:93–99
121. Chen L, Zhu K, Bi L-H, Suchopar A, Reicke M, Mathys G, Jaensch H, Kortz U, Richards RM (2007) Inorg Chem 46:8457–8459
122. Bianchi D, Bortolo R, Tassinari R, Ricci M, Vignolo R (2000) Angew Chem 112:4491–4493, Angew Chem Int Ed 39:4321–4323
123. Molinari R, Poerio T, Argurio P (2006) Catal Today 118:52–56
124. Liu H, Fu Z, Yin D, Yin D, Liao H (2005) Catal Commun 6:638–643
125. Taktak S, Flook M, Foxman BM, Que L, Rybak-Akimova EV (2005) Chem Comm 5301–5303
126. Oh NY, Seo MS, Lim MH, Consugar MB, Park MJ, Rohde J-U, Han J, Kim KM, Kim J, Que L, Nam W (2005) Chem Comm 5644–5646
127. de Visser SP, Oh K, Han A-R, Nam W (2007) Inorg Chem 46:4632–4641
128. Thibon A, Bartoli J-F, Guillot R, Sainton J, Martinho M, Mansuy D, Banse F (2008) J Mol Catal A Chem 287:115–120
129. Kudrik EV, Sorokin AB (2008) Chem Eur J 14:7123–7126
130. Kang M-J, Song WJ, Han A-R, Choi YS, Jang HG, Nam W (2007) J Org Chem 72: 6301–6304
131. Quintanilla A, Casas JA, Zazo JA, Mohedano AF, Rodríguez JJ (2006) Appl Catal B Environ 62:115–120
132. Abussaud BA, Ulkem N, Berk D, Kubes GJ (2008) Ind Eng Chem Res 47:4325–4331
133. Giri NG, Chauhan SMS (2009) Catal Commun 10:383–387
134. Çimen Y, Türk H (2008) Appl Catal A Gen 340:52–58
135. Zalomaeva OV, Sorokin AB (2006) New J Chem 30:1768–1773
136. Kholdeeva OA, Zalomaeva OV, Sorokin AB, Ivanchikova ID, Della Pina C, Rossi M (2007) Catal Today 121:58–64
137. Shul'pina L, Veghini D, Kudinov AR, Shul'pina GB (2006) React Kinet Catal Lett 88: 157–163
138. Wang N, Liu R, Chen J, Liang X (2005) Chem Commun 5322–5324
139. Pearson AJ, Kwak Y (2005) Tetrahedron Lett 46:5417–5419
140. Namboodiri VV, Polshettiwar V, Varma RS (2007) Tetrahedron Lett 48:8839–8842
141. Shi F, Tse MK, Li Z, Beller M (2008) Chem Eur J 14:8793–8797
142. Ghosh A, Tiago de Oliveira F, Yano T, Nishioka T, Beach ES, Kinoshita I, Münck E, Ryabov AD, Horwitz CP, Collins TJ (2005) J Am Chem Soc 127:505–2513
143. Oh NY, Suh Y, Park MJ, Seo MS, Kim J, Nam W (2005) Angew Chem 117:4307–4311, Angew Chem Int Ed 44:4235–4239
144. Han JH, Yoo S-K, Seo JS, Hong SJ, Kim SK, Kim C (2005) Dalton Trans 402–406

145. Kumar A, Jain N, Chauhan SMS (2007) Synlett 411–414
146. Huang J-Y, Li S-J, Wang Y-G (2006) Tetrahedron Lett 47:5637–5640
147. Geraskin IM, Luedtke MW, Neu HM, Nemykin VN, Zhdankin VV (2008) Tetrahedron Lett 49:7410–7412
148. González-Arellano C, Campelo JM, Macquarrie DJ, Marinas JM, Romero AA, Luque R (2008) ChemSusChem 1:746–750
149. Han H, Zhang S, Hou H, Fan Y, Zhu Y (2006) Eur J Inorg Chem 1594–1600
150. Nagaraju P, Pasha N, Prasad PSS, Lingaiah N (2007) Green Chem 9:1126–1129