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Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substrates with Molecular Oxygen

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1. Introduction

Catalytic oxidation is a key technology for converting petroleum-based feedstocks to useful chemicals of a high oxidation state such as alcohols, carbonyl compounds, and epoxides. Millions of tons of these compounds are annually produced worldwide and find applications in all areas of chemical industries, ranging from pharmaceutical to large-scale commodities.[1] For economic and environmental reasons, the oxidation processes of bulk chemical industries predominantly involve the use of molecular oxygen as the primary oxidant. Their success depends largely on the use of metal catalysts to promote both the rate of reaction and the selectivity to partial oxidation products. The production of ethylene oxide from ethylene with molecular oxygen catalyzed by silver salts,[2] that of terephthalic acid from p-xylene using molecular oxygen in the presence of manganese and

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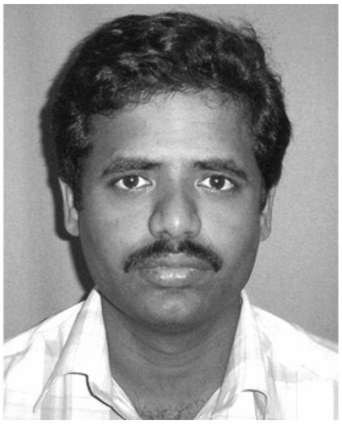
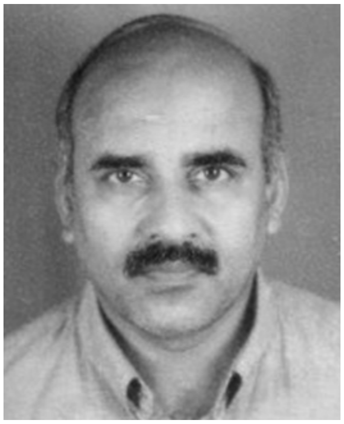
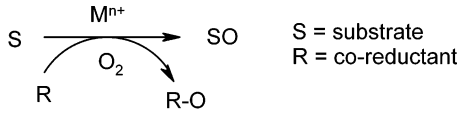


Subbarayan Velusamy was born in 1979 at Karur, India. After receiving his M.Sc. degree in 2001 from the Department of Organic Chemistry, University of Madras, he joined Dr. Punniyamurthy's research group at the Department of Chemistry, Indian Institute of Technology Guwahati for Ph.D. work. His research interests are green chemistry, asymmetric synthesis, and synthesis of natural and unnatural compounds.

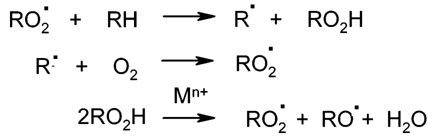


Javed Iqbal, after graduating from Delhi University in 1977, went to Cambridge University to work as a postdoctoral fellow with Prof. Ian Fleming, FRS. He subsequently moved to Oxford University in 1982 as a fellow of Wolfson College and worked with Prof. Sir J. E. Baldwin, FRS, on penicillin biosynthesis. After teaching for a year at the University of Montpellier, France, he returned to India in 1984 and joined IIT Kanpur as a faculty member in the Department of Chemistry and became a professor there in 1990. He made a switch from academia to industry and joined Dr. Reddy's Research Foundation, Hyderabad, India, as senior vice president of research in the year 2000. After spending a year as Director of Regional Research Laboratory (CSIR), Trivandrum, India, he came back to Dr. Reddy's Laboratories Ltd. in January 2003 and was given the title of Distinguished Research Scientist and Global Head of Discovery Chemistry. He has 25 years of teaching and research experience and has 110 research publications in international journals. He also holds 10 global patents on new drug molecules. He has guided 12 Ph.D. and 30 M.Sc. students at IIT Kanpur. He was a visiting professor at the University of Notre Dame, Indiana (1989–1990), and the University of Okayama, Japan (1994). He has also taught at New Mexico State University during 1997–2000 in the summer semesters. He is a fellow of the Indian Academy of Science, Bangalore, and the Indian National Science Academy, New Delhi. His research interests include synthetic organic chemistry and discovery of new drugs in the area of diabetes, cancer, and cardiovascular diseases.

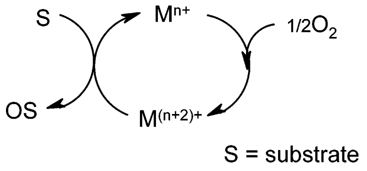
Scheme 1



Scheme 2



Scheme 3



cobalt salts,[3] and the Wacker oxidation of alkenes to carbonyl compounds catalyzed by palladium salts[1k] are examples of successful commercial processes.

During recent years, in the wake of increasingly stringent environmental legislation, attention has also been focused on the development of catalytic oxidations for the manufacture of fine chemicals. The traditional methods of many fine chemical oxidations involve stoichiometric quantities of toxic inorganic reagents such as permanganate and dichromate. These reactions generate large amounts of inorganic salt-containing effluent along with the target products. Thus, currently there is considerable pressure to replace these antiquated technologies with cleaner, catalytic alternatives. A clean synthetic technology that should proceed with a high atom economy and the overall synthesis must be accomplished with a low E-factor, thereby minimizing the cost of waste disposal.[1f] The ideal system for "green" oxidation is the use of molecular oxygen as the primary oxidant together with recyclable catalysts in nontoxic solvents or supercritical CO_2.[1e] Thus, the current goal of the research and industry is the development of effective metal catalysts that can activate the molecular oxygen at ambient conditions and transfer to fine chemical substrates with high stereoselectivity.

The aerobic catalytic oxidations, irrespective of heterogeneous or homogeneous process, can be classified into four categories as described below:

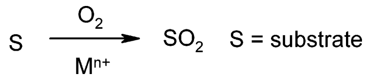
(i) Oxidation Based on the Model of Monooxygenase. These oxidations are modeled on the natural monooxygenase and require coreductants such as RCHO, ROH, and PPh_3 (Scheme 1).[4a−e]

(ii) Free Radical Oxidation. These oxidations are generally carried out without any external coreductant and more closely resemble autoxidation than monooxygenase-catalyzed systems (Scheme 2).[5]

(iii) Oxidation of a Coordinated Substrate by a Metal Ion. In this oxidation, the oxidized form of the metal is subsequently regenerated by reaction of the reduced form with molecular oxygen (Scheme 3).[1k,6,7e]

(iv) Oxidation Mimicking Dioxygenase. In this reaction both oxygen atoms of the activated molecular oxygen coordinated to the transition metal complex are incorporated into the substrate (Scheme 4).[4f]

Scheme 4



This review covers the recent advances of the aerobic epoxidation of alkenes, oxidation of alkenes to alcohols and ketones, Wacker oxidation, allylic oxidation, C−H oxidation, Baeyer−Villiger oxidation, and sulfoxidation reactions. The aerobic oxidation of alcohols to carbonyl compounds is not covered in this contribution because it has been very recently reviewed.[6] Thus, section 2 is devoted to epoxidation, whereas section 3 presents the oxidation of alkenes to alcohols and ketones. Wacker oxidation and allylic oxidation of alkenes are discussed in sections 4 and 5, respectively, whereas sections 6 and 7 give a survey of the oxidative dehydrogenation and oxygenation of alkanes. Benzylic oxidation, aromatic C−H oxidation, Baeyer−Villiger oxidation, and sulfoxidation reactions are covered in sections 8−11, respectively. All of the processes that use transition metal complexes as the catalysts with molecular oxygen have been considered.

Several books and review articles have appeared, which are wholly or partly devoted to the metal-catalyzed aerobic oxidations.[7] Reviews and books devoted to more narrow topics will be cited later. Consequently, the present paper emphasizes the works published during the past 10−15 years. Due to a vast literature, the reviews are cited rather than original publications in some cases. This review covers studies up to September 2004.

2. Epoxidation

Epoxides are important synthetic intermediates for the synthesis of oxygen-containing natural and unnatural compounds.[7f,8] Access to a variety of epoxides has largely been successful due to the remarkable catalytic activity of transition metal complexes, which have a unique ability to bring the alkene substrate and the oxygen source within the coordination sphere of the metal leaving to a facial transfer of oxygen atom to the carbon−carbon double bond. This section describes the role of various transition metal complexes used during the epoxidation with molecular oxygen.

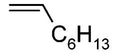
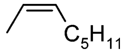
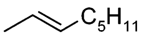
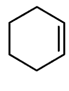
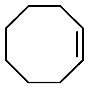
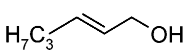
2.1. Titanium Catalysts

Silica-supported titanium catalysts are investigated for the epoxidation of propene with molecular oxygen at 200−300 °C.[9] The catalyst having titanium-modified silica zeolite with an Si/Al ratio of 1900 is found to be the most effective, affording propene oxide in 20.4% yield at 300 °C.[9d] It is expected that fine control of acid properties of the supports and titanium content may enhance the catalyst performance for propene oxide formation.

2.2. Vanadium and Molybdenum Catalysts

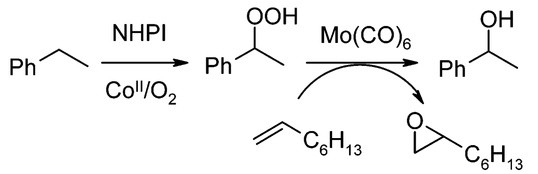
These catalysts have been studied for the aerobic epoxidation of alkenes in the presence as well as absence of coreductants.

Table 1. Epoxidation of Alkenes Using NHPI, $Co(OAc)_2$, and $Mo(CO)_6$[a]

entry	substrate	conversion (%)	selectivity (%)
1		38	80
2		83	88
3		78	87
4		80	74
5		89	83
6		97	92

[a] Alkene (4 mmol) and ethylbenzene (40 mmol) were stirred with 1 atm of O_2 in the presence of NHPI (10 mol %), $Co(OAc)_2$ (0.1 mol %), $Mo(CO)_6$ (5 mol %), and MS 4Å (200 mg) in PhCN (2 mL) for 14 h at 50−70 °C.

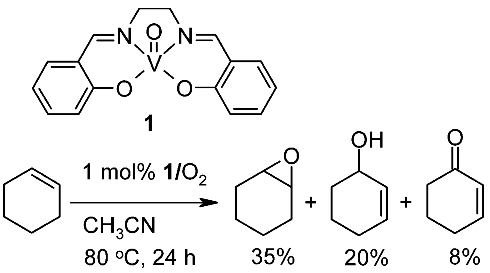
Scheme 5



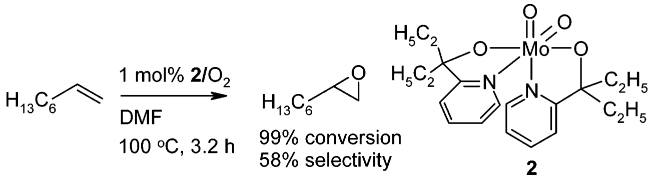
2.2.1. Reactions without Coreductants

Vanadium- and molybdenum-based catalysts have been widely used for the epoxidation of alkenes with hydroperoxides.[10a] Consequently, the development of an epoxidation system using a hydroperoxide generated in situ by autoxidation is attractive from the synthetic and industrial point of view. Thus, the epoxidation of a variety of alkenes has been described by the combined use of *N*-hydroxyphthalimide (NHPI), $Co(OAc)_2$, $Mo(CO)_6$, and ethylbenzene in the presence of molecular oxygen (Table 1).[10b] This reaction involves autoxidation of ethylbenzene assisted by NHPI and the subsequent epoxidation of alkenes with the resulting hydroperoxide catalyzed by $Mo(CO)_6$ (Scheme 5). Similarly, the Keggin-type polyoxometalates, $PTMM_{11}O_{39}{}^{4-}$ (TM = Mn^{II}, Co^{II}, or Ru^{III} and M = Mo^{VI} or W^{VI}), have been shown to catalyze the autoxidation of cumene to cumylhydroperoxide with molecular oxygen that transfers one oxygen atom to 1-octene to provide the corresponding epoxide in high turnover number (TON),[10c] whereas the vanadium and molybdenum complexes **1**−**3** have been used for the epoxidation of cyclohexene, 1-octene, and styrene, respectively (Schemes 6 and 7).[10d−f] These reactions operate with moderate selectivity in the presence of molecular oxygen at 50−100 °C. The catalyst **3** has been encapsulated on zeolite (NaY) to afford **3**−NaT, which catalyzes the epoxidation of styrene with high yield (Scheme 8).[10f] The catalytic activity and selectivity of **3**−NaY is significantly higher than that of its homogeneous analogue **3**.

Scheme 6



Scheme 7



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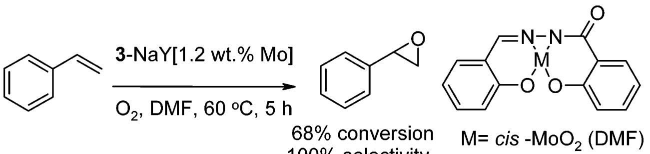
Scheme 8



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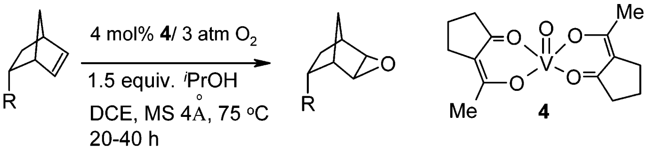
2.2.2. Reactions Involving Coreductants

Vanadium-based catalysts have been used for the aerobic epoxidation of alkenes in the presence of coreductants. Mukaiyama and co-workers reported the epoxidation of norbornene derivatives using vanadium complex **4** and molecular oxygen in the presence of 2-propanol (Scheme 9).[11] Addition of molecular sieves (4 Å) is essential to this reaction, as in their absence the catalyst **4** becomes less active, leading to a low yield of the epoxide. The polyoxometalate, NPV_6Mo_6, catalyzes the epoxidation of a variety of alkenes including homoallylic alcohols in the presence of aldehydes at ambient conditions (Scheme 10).[12] Aliphatic aldehydes bearing di- or trialkyl groups on the α-position of the carbonyl carbon are found to be effective for this system.

2.3. Manganese Catalysts

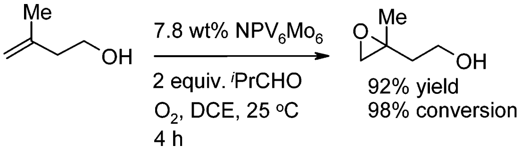
Manganese complexes catalyze the epoxidation of unfunctionalized alkenes with molecular oxygen.

Scheme 9

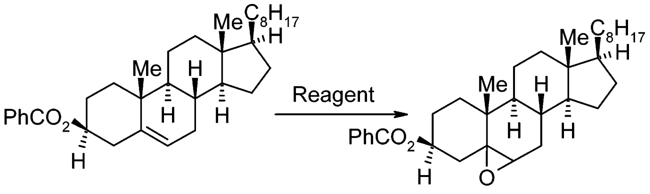


R-Group	Yield (%)
H	78
$PhCO_2CH_2$	63
$PhCO_2CHCH_3$	68

Scheme 10



Scheme 11



Reagent	Yield (α:β)
$Mn(dpm)_2/O_2/{}^{i}PrCHO$	82% (20:80)
m-CPBA	76% (71:29)

Most of these reactions function in the presence of coreductants.

2.3.1. Reactions with Achiral Catalysts

Mukaiyama and co-workers reported the epoxidation of cholesteryl derivatives using $Mn(dpm)_2$ (dpm = dipivaloylmethanato) in the presence of 2-methylpropanal and molecular oxygen (Scheme 11).[13a] This result is of particular interest because the stereoselectivity of the cholesteryl epoxide is opposite (β-epoxide) to that observed using a peracid (α-epoxide) such as *m*-chloroperbenzoic acid.[13b] The reverse stereoselectivity suggests that the epoxidation with $Mn(dpm)_2$ is not a process involving a simple carboxylic peracid generated from the aldehyde by autoxidation; rather, an oxygenated metal complex is the reactive intermediate.

The epoxidation of a variety of unfunctionalized alkenes has been subsequently performed using manganese catalysts in the presence of coreductants. Manganese porphyrin complexes,[14] $Mn(OAc)_2$[15], and complex **5**[16] have been employed for the epoxidation of a wide range of alkenes in the presence of aldehydes and molecular oxygen. Investigation of **5** reveals that it exists as a monomer and does not undergo dimerization through the formation of a μ-oxobridge[17a] or oxidative degradation via the formation of a multinuclear μ-oxo complex[17b] during the reaction processes due to steric hindrance.[17c] Nolte and Gosling reported a two-phase system utilizing MnTPPCl **6** (TPP = 5,10,15,20-tetraphenylporphyrinato) and [Rh(III)bipyCp*Cl]Cl (bipy = 2,2′-bipyridine; Cp* = η^5-C_5Me_5) with sodium formate for the reductive activation of molecular oxygen and the subsequent epoxidation of alkenes.[18] The reducing equivalents for the conversion of Mn^{III} to Mn^{II} are obtained from the rhodium-catalyzed oxidation of formate to CO_2 (Scheme 12). The complex **6** has also been used for the epoxidation of cyclohexene in the presence of zinc powder as a reductant and benzoic anhydride as a cleaving agent of the molecular oxygen.[19]

Scheme 12

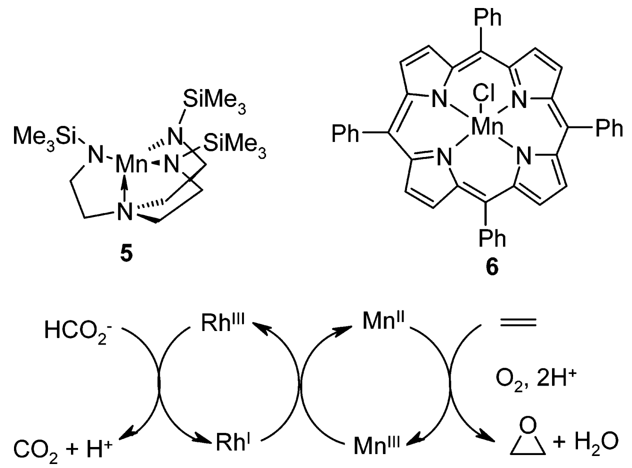


Table 2. Aerobic Epoxidation of Alkenes Using MAlPO (M = Co or Mn)[a]

entry	substrate	catalyst	conversion (%)	selectivity (%)	
				epoxide	diol
1	styrene	MnAlPO-36	46	34	59
		MnAlPO-5	32	49	60
		CoAlPO-36	46	34	59
2	cyclohexene	MnAlPO-36	62	77	19
		MnAlPO-5	44	77	13
		CoAlPO-36	54	69	27
		CoAlPO-5	47	74	15
3	α-pinene	MnAlPO-36	59	91	
		MnAlPO-5	42	66	
4	(+)-limonene	CoAlPO-36	54	84	
		CoAlPO-5	32	55	
5	1-hexene	MnAlPO-36	51	87	
		MnAlPO-5	30	51	
		CoAlPO-36	46	78	
		CoAlPO-5	28	39	
		MnAlPO-18	43	91	
		CoAlPO-18	37	87	27

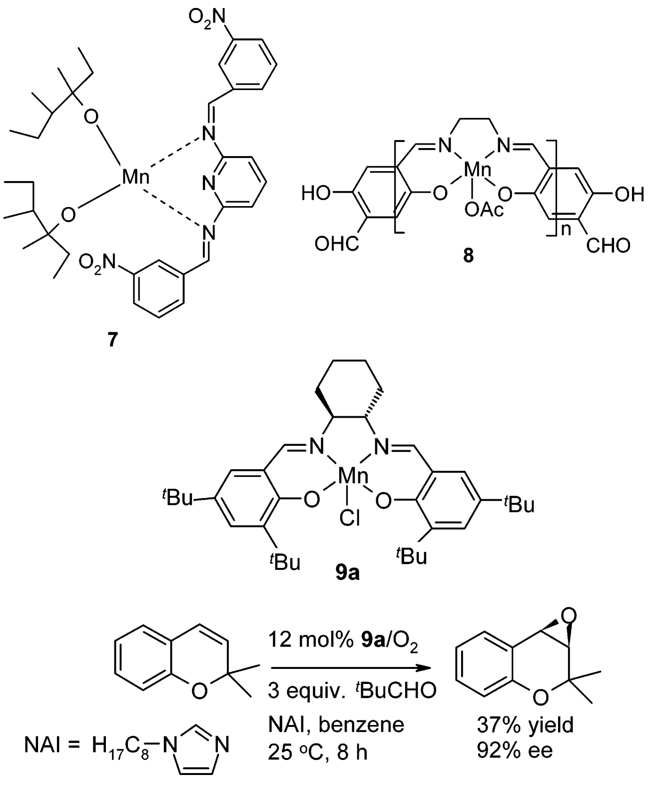
[a] Substrate (35 g), benzaldehyde (3 mol equiv with respect to substrate), and catalyst (0.25 g) were stirred at 50 °C under 30 atm of air for 4−24 h.

Few studies have focused on the use of solid supported and polynuclear manganese catalysts. Manganese aluminophosphates, MnAlPO-5, MnAlPO-18, and MnAlPO-36, have been shown to catalyze the production of acylperoxy radicals from benzaldehyde; these, in turn, in dry air (30 atm) convert cyclohexene, styrene, α-pinene, (+)-limonene, and 1-hexene to a mixture of epoxides and diols in high yields (Table 2).[21] Other aldehydes can be used as sacrificial oxidants for this system provided they are small enough to gain access to the active sites situated at the inner surface of the molecular sieve catalyst. Importantly, the manganese ions are not leached out during the use. The polymeric manganese Schiff base **8** has been subsequently used for the epoxidation of cyclohexene, 1-hexene, 1-octene, styrene, and cyclooctene in the presence of 2-methylpropanal at ambient conditions,[22] whereas the protocol employing zeolite−NaY-encapsulated Mn−Schiff base complex **7** catalyzes the epoxidation of 1-octene and 1-decene in 26−63% conversion (74−75% selectivity) under oxygen atmosphere.[20] This is the first example in the manganese-catalyzed aerobic epoxidation of alkenes that functions without a coreductant.

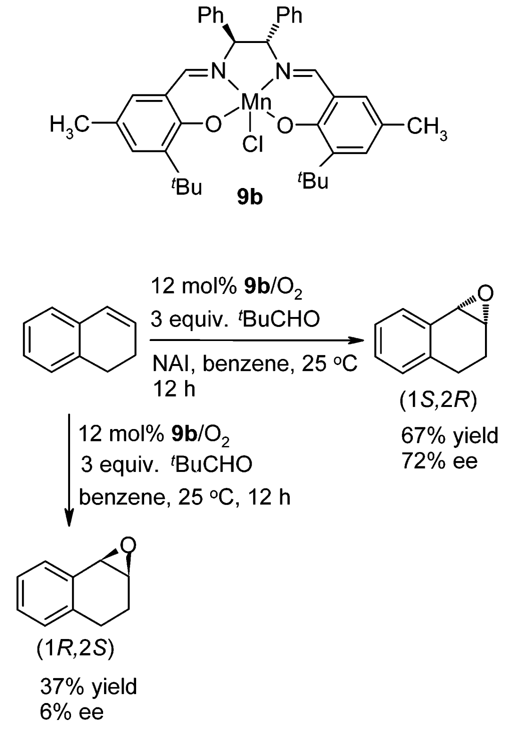
2.3.2. Enantioselective Reactions

The enantioselective epoxidation of unfunctionalized alkenes is a highly successful reaction using chiral Mn−salen complexes **9** in the presence of α-branched aliphatic aldehydes[23a−e] and β-ketoesters[23f] (Scheme 13). Addition of *N*-alkylimidazole (NAI) is essential in these reactions as its absence leads to

Scheme 13

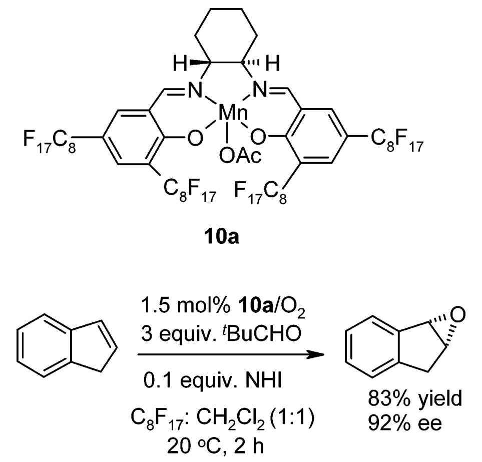


Scheme 14

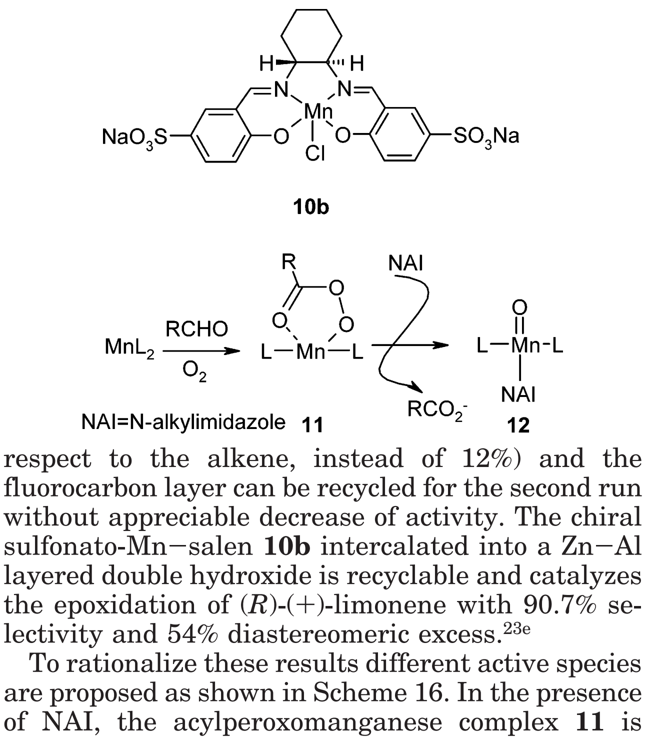


low chemical and optical yield of an epoxide having the opposite enantioselectivity (Scheme 14). Additives of such kind are supposed to act as additional ligands in the axial position to the metal center. These reactions are also found to be effective in a fluorous biphase system (FBS), and up to 92% ee is reported in the epoxidation of indene using complex **10a** (Scheme 15).[23d] The FBS needs a substantially lower amount of the catalyst compared with those required under homogeneous conditions (catalyst 1.5% with

Scheme 15



Scheme 16



respect to the alkene, instead of 12%) and the fluorocarbon layer can be recycled for the second run without appreciable decrease of activity. The chiral sulfonato-Mn–salen **10b** intercalated into a Zn–Al layered double hydroxide is recyclable and catalyzes the epoxidation of (*R*)-(+)-limonene with 90.7% selectivity and 54% diastereomeric excess.[23e]

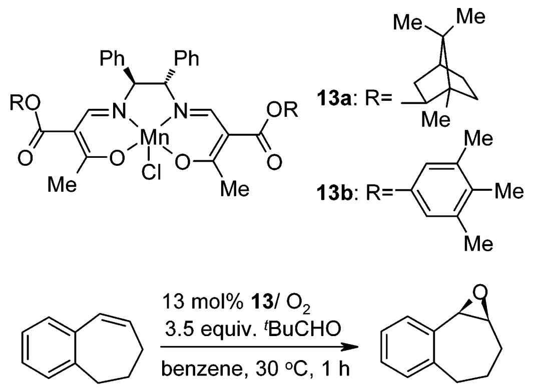
To rationalize these results different active species are proposed as shown in Scheme 16. In the presence of NAI, the acylperoxomanganese complex **11** is transformed to the oxomanganese complex **12**, an intermediate that is in accordance with the one proposed in the Jacobsen–Katsuki epoxidation which leads to the (1*S*,2*R*)-enantiomer of the epoxide.[24a–c] However, in the absence of NAI, **11** leads to the formation of the (1*R*,2*S*)-epoxide.[24d]

Changing the ligand structure from salen to optically active *β*-ketoimine-type ligands afforded **13**, which catalyzes more efficiently the epoxidation of 1,2-dihydronaphthalene, conjugated dienes, and enynes in high enantioselectivity (up to 87% ee) in the presence of pivalaldehyde and molecular oxygen in benzene (Scheme 17).[25] The enantioface selection is opposite from those obtained by using terminal oxidants such as NaOCl and PhIO. Thus, the formation of an acylperoxomanganese complex such as **11** from **13** is proposed for this system.

2.4. Iron Catalysts

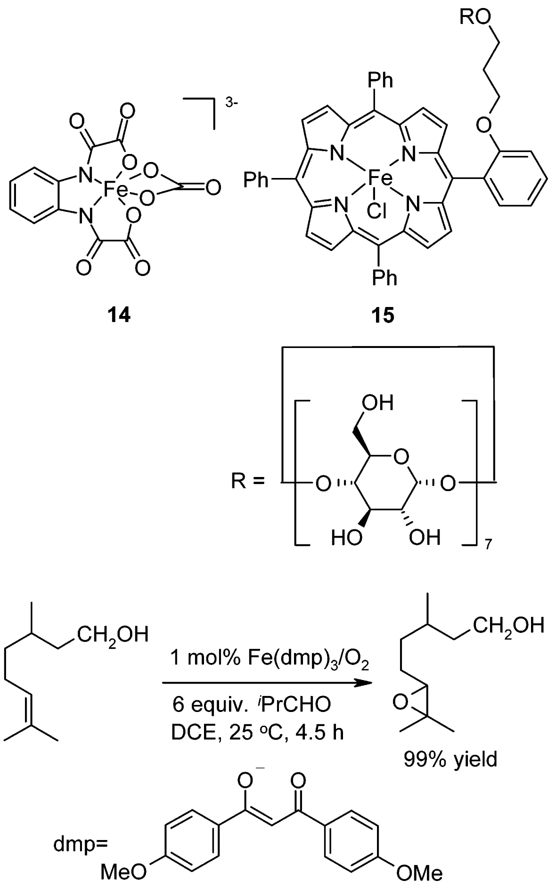
Iron complexes are considered to be one of the most promising catalysts for oxygenation, because iron is

Scheme 17



Catalyst	Yield (%)	ee (%)
13a	52	84
13b	43	76

Scheme 18



an inexpensive and less hazardous metal compared with other transition metals. Therefore, much research work has been conducted for iron complex catalyzed epoxidation of alkenes with various oxidants: PhIO,[26a] NaOCl,[26b] perbenzoate,[26c] and molecular oxygen.[26d,e] During recent years, $Fe(dmp)_3$ [dmp = 1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato],[27] $Fe(AAEMA)_3$ [AAEMA = 2-(acetoacetoxy)ethyl methacrylate],[28] and iron(III) oxamato complex[29] **14** have been investigated for the epoxidation of a variety of cyclic and linear alkenes in the presence of 2-methylpropanal and molecular oxygen. By this method, olefinic alcohols can be converted to the corresponding epoxy alcohols in quantitative yield (Scheme 18).

Hennig and co-workers studied the photocatalytic oxidation of cycloalkenes with molecular oxygen and iron(III) porphyrin complexes.[30] Alkenes with strained carbon−carbon double bonds give preferentially epoxides, whereas mainly allylic oxidation is observed for unstrained alkenes. Enantioselective photooxygenation of racemic α-pinene is investigated using the cyclodextrin-linked iron−porphyrin complex **15** in the presence of 2-methylpyridine in benzene to afford a mixture of epoxides (41% ee), allylic alcohols (49−67% ee), and enones (5−23% ee). In this reaction, 2-methylpyridine is believed to make axial complexation with the metal center at the unprotected side of the porphyrin, lowering the participation of oxygenation reactions by the “achiral site” of **15**.

2.5. Ruthenium Catalysts

Ruthenium-catalyzed epoxidation has been carried out by a wide variety of ligands. Most of these oxidations proceed via a labile ruthenium oxo species, which transfers the oxygen atom to the organic substrates.

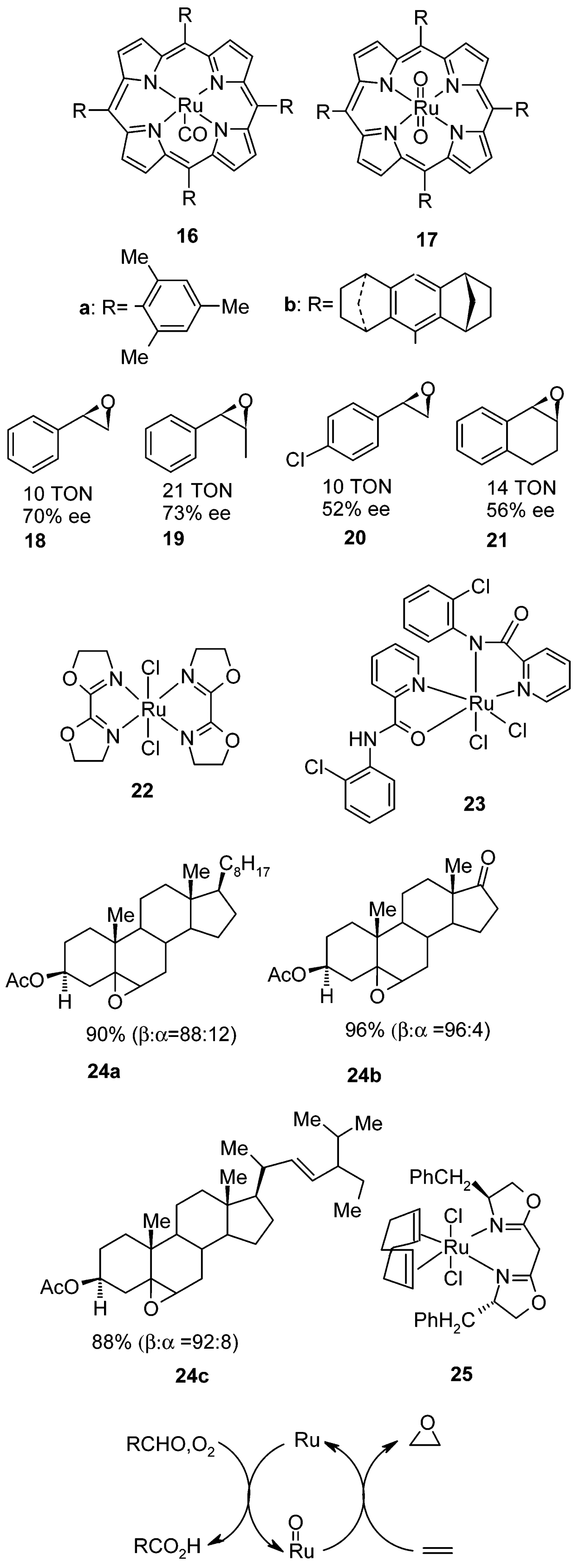
2.5.1. Reactions without Coreductants

The use of oxoruthenium complexes as the catalysts for the oxidation of organic substrates has been the subject of intense study in recent years.[31] A ruthenium complex, $Ru(TMP)O_2$ **17a** (TMP = tetramesitylporphyrinato), prepared by *m*-CPBA oxidation of the corresponding carbonyl−Ru(II) complex, Ru(TMP)CO **16a**, is used by several groups for the epoxidation of wide range of alkenes with up to 40 TON in the presence of molecular oxygen.[32] Che and co-workers described that the chiral ruthenium complex **17b** catalyzes the oxidation of styrene derivatives and 1,2-dihydronaphthalene to epoxides **18**−**21** (up to 73% ee) under 8 atm of molecular oxygen.[33] This is the first example of the aerobic enantioselective epoxidation of alkenes that does not rely on the use of a coreductant. Neumann and Dahan reported that the ruthenium-based polyoxometalate, $[WZnRu^{III}_2(ZnW_9O_{34})_2]^{11-}$ catalyzes the epoxidation of a wide range of alkenes with up to 120 TON under molecular oxygen.[34]

2.5.2. Reactions Involving Coreductants

Ruthenium complexes have been shown to catalyze efficiently the epoxidation of alkenes in the presence of 2-methylpropanal at ambient conditions.[35−37] Thus, the epoxidation of a variety of cyclic alkenes has been carried out using catalysts **22** and **23** in high yields (Scheme 19).[35a,b] Steroids are mainly converted to the corresponding *β*-epoxides **24a**−**c**.[35a] Knochel and Ragagnin reported that $RuCl_3$−pyridine−benzimidazole catalyzes the epoxidation of alkenes including steroids in a fluorous biphase system (FBS).[35c] The fluorous phase containing the catalyst can be recycled without loss of activity. The chiral ruthenium complexes, (*S*,*S*)-ruthenium(II) bisoxazole[36] **25** and [brucine](*R*)-Ru(III)(PDTA-H)Cl][37] (PDTA = propylene-1,2-diaminotetraacetic acid) **26**, have been used for

Scheme 19



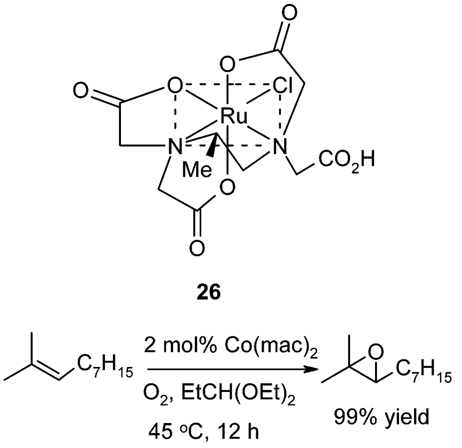
the epoxidation of styrene derivatives, where **26** is found to be efficient in providing the epoxides with up to 57% ee (Table 3).[37] These preliminary results suggest that chiral ruthenium complexes may lead to effective catalytic systems for the enantioselective epoxidation of unfunctionalized alkenes.

Table 3. (*R*)-Ru(III) PDTA 22 Catalyzed Aerobic Enantioselective Epoxidation of Unfunctionalized Alkenes[a]

entry	substrate	conversion (%)	ee (%)
1	styrene	64	43
2	4-chlorostyrene	58	38
3	4-nitrostyrene	50	28
4	4-methylstyrene	68	48
5	1,2-dihydronaphthalene	76	57
6	indene	57	48

[a] Alkene (2 mmol), catalyst (0.006 mmol), and 2-methylpropanal (6 mmol) were stirred in 1:1 1,4-dioxane and water (1.5 mL) under 1 atm of O_2 at pH 7−8 at 4 °C for 24 h.

Scheme 20

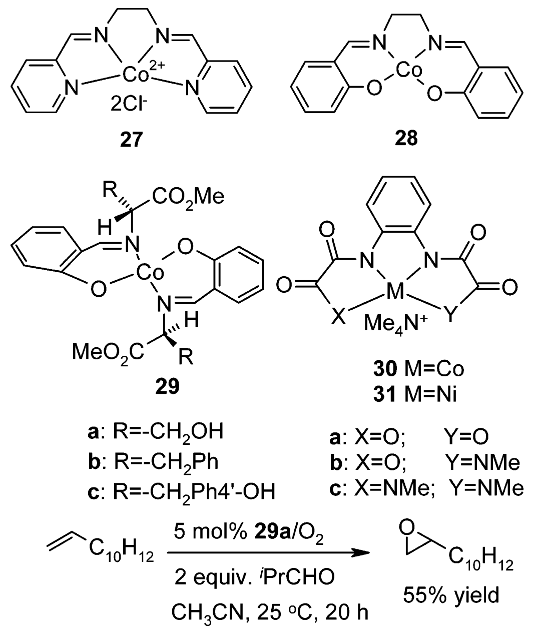


2.6. Cobalt Catalysts

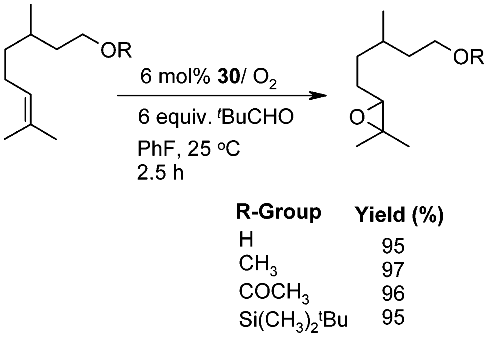
Cobalt-catalyzed epoxidation of alkenes with molecular oxygen is extensively investigated. Most of these reactions have been performed in the presence of coreductants such as aldehydes, acetals, and *β*-ketoesters. Cobalt(II) complexes containing *β*-diketone ligands with electron-donating substituents have been shown to catalyze the epoxidation of alkenes in the presence of diethyl acetal[38] and 2-methylpropanal.[39] Because the protocol involving diethyl acetal functions under neutral conditions, epoxidation of acid sensitive alkenes can be performed (Scheme 20).[38a] Iqbal and co-workers studied the Schiff base complexes **27**−**29** for the epoxidation of alkenes including steroids and terpenoids in the presence of either aliphatic aldehyde or *β*-ketoester at ambient temperature (Scheme 21).[40] Journax and co-workers reported that square-planar cobalt(III) complexes **30** catalyze the epoxidation of alkenes in moderate to high yields in the presence of pivalaldehyde at ambient temperature.[41] Alkenes bearing hydroxy and ether groups are converted to the corresponding epoxides without undesirable decomposition of the functional groups (Scheme 22). Contrary to the case of analogous Collins complexes,[42] no epoxidation is observed with PhIO.

There are few studies focusing on the use of polymer and solid supported cobalt catalysts for the aerobic epoxidation of alkenes in the presence of aldehydes.[43,44] Iqbal and co-workers employed the polyaniline-supported Co−salen **28** for the *π*-facial selective epoxidation of *N*-cinnamoyl amino acid

Scheme 21



Scheme 22



Scheme 23

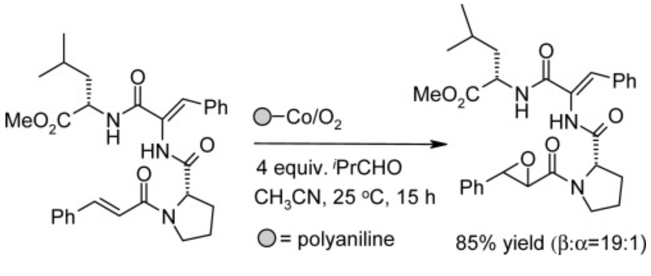
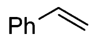
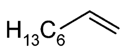
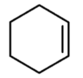
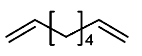
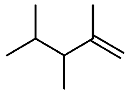
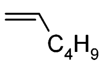


Table 4. Epoxidation of Alkenes Using 32 (Reprinted with Permission from Reference 44b. Copyright 1996 Royal Society of Chemistry)[a]

entry	substrate	time (h)	yield (%)
1		3	32[b]
2		5	45
3		5	85
4		24	48[c]
5		5	95
6		24	30

[a] All reactions were carried out at 19 °C in CH_2Cl_2 with 2-methylpropanal and under atmospheric oxygen. [b] 5% of benzaldehyde and 21% of polymer obtained. [c] 7% of diepoxide formed.

derivatives in the presence of 2-methylpropanal and molecular oxygen (Scheme 23).[43] The peptides that are able to adopt a γ- or β-turn due to intramolecular hydrogen bonding provide high diastereoselectivity. Under similar conditions, the polybenzimidazole **32** supported $Co(acac)_2$[44a] and silica-supported cobalt–carboxylate[44b] **33** catalyze the epoxidation of a variety of unfunctionalized alkenes with high yields (Table 4). Cobalt aluminophosphates (CoAlPO) have been shown to catalyze the epoxidation of cyclohexene, styrene, α-pinene, (+)-limonene, and 1-hexene in the presence of benzaldehyde and molecular oxygen (Table 2).[21] The catalytic activity of CoAlPO is comparable with the corresponding MnAlPO in terms of the selectivity and yield of the epoxide. However, the reaction involving the zeolite (NaX) supported $Co(OAc)_2$ catalyzes the epoxidation of styrene with 44.2% conversion and 60% selectivity under oxygen atmosphere.[45] This is the first example in the cobalt-catalyzed aerobic epoxidation of alkenes that does not involve a coreductant.

2.7. Iridium Catalysts

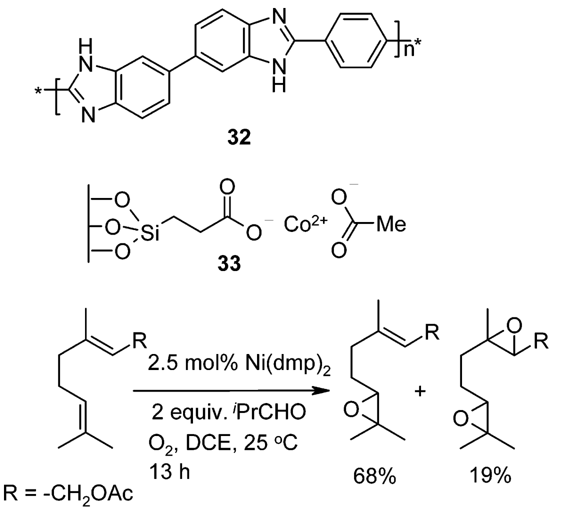
Takao and co-workers investigated the oxidation of styrene into a mixture of styrene epoxide, benzaldehyde, and acetophenone by Vaska's complex, $IrCl(CO)(PPh_3)_2$, in toluene at 110 °C.[46] Cyclohexene and 1-hexene have been oxidized into a mixture of the corresponding epoxides, enols, and enones in the presence of $[Ir(CH_3CN)_4NO_2](X)_2$ (X = PF_6 or BF_4) at 120 °C under 20 atm of molecular oxygen.[47]

2.8. Nickel Catalysts

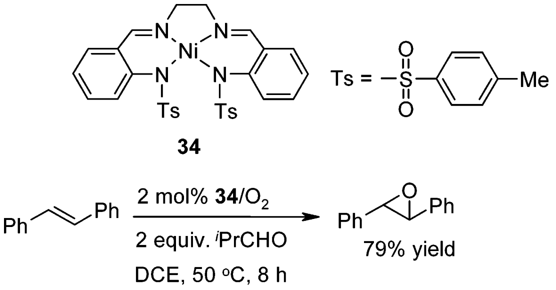
Nickel complexes have been widely studied for the aerobic epoxidation of alkenes. Mukaiyama and co-workers reported the epoxidation of a variety of alkenes using $Ni(dmp)_2$ [dmp = 1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato] in the presence of 2-methylpropanal[48] and *n*-butanol[49] (Scheme 24). The reaction involving the alcohol needs an excess of the catalyst, oxygen pressure, and heating compared to the process of the aldehyde. Katsuki and co-workers described the epoxidation of linear alkenes using **34** in the presence of 2-methylpropanal and molecular oxygen (Scheme 25).[50] The square planar nickel(II) complexes **31** have been shown to catalyze the epoxidation of 1,2-dihydronaphthalene, indene, *trans*-stilbene, β-methylstyrene, and β-citronellol derivatives in the presence of 2-methylpropanal and molecular oxygen,[51] whereas the chiral nickel complex **35** catalyzes the epoxidation of 1-octene, indene, 1-hexene, and *tert*-4-octene with 18–41% ee and 66–85% yield.[52]

Polymer and solid supported nickel complexes have been studied for the epoxidation of a wide range of alkenes. The clay-impregnated nickel complex, $Ni(acac)_2$-montmorillonite K10, is used for the epoxi-

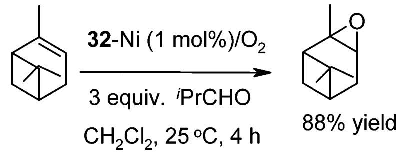
Scheme 24



Scheme 25



Scheme 26



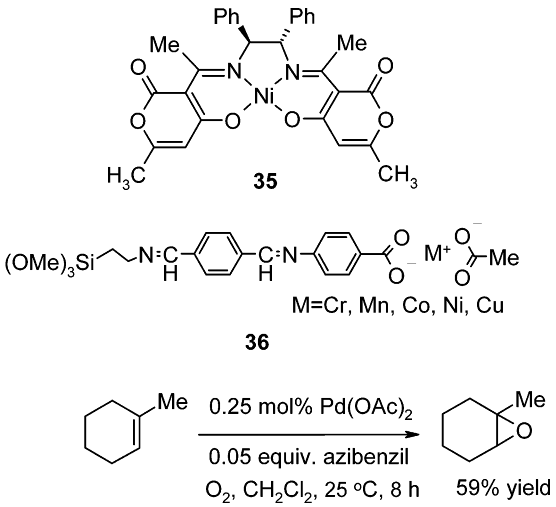
dation of a variety of alkenes in the presence of 2-methylpropanal and compressed air.[53] Under similar reaction conditions, the nickel carboxylate anchored on mesoporous silica **36**[54] and the polybenzimidazole **32** supported Ni(acac)$_2$[44a] catalyze the epoxidation of cyclohexene, (*S*)-limonene, α-pinene, 1-octene, and styrene in high yields (Scheme 26). The polymer-bound complex **32**−Ni(acac)$_2$ can be recovered from the reaction mixture. However, some loss of activity is observed upon reuse of the catalyst, presumably due to leaching of the metal complex.

2.9. Palladium Catalysts

Pd(OAc)$_2$ is used for the epoxidation of unfunctionalized alkenes with molecular oxygen in the presence of azibenzil (Scheme 27).[55] Accordingly, the cyclic and terminal aliphatic alkenes are selectively epoxidized in moderate to good yields, and internal alkenes afford a mixture of *cis* and *trans* epoxides. However, in the case of aromatic alkenes, oxidative cleavage of the carbon−carbon double bond is reported.

The epoxidation of propene catalyzed by Pd−Pt/TS-1 with in situ formed hydrogen peroxide from molecular oxygen and hydrogen is reported in a fixed bed reactor under high-pressure conditions.[56a] The initial propene oxide selectivity is very high (99%) at 3.5% conversion, but the catalyst deactivates rapidly with time-on-stream, and successively the formation of methyl formate becomes the prevalent reaction. Use of CO$_2$, instead of N$_2$, has a beneficial effect on the formation of propene oxide, and even higher yields are obtained when the pressure is increased from 49 to 118 atm (supercritical fluid phase). Alternatively, Pd(OAc)$_2$ has been shown to catalyze the epoxidation of propene in 42.7% conversion and 81.6% selectivity in the presence of molecular oxygen.[56] This reaction operates in the presence of cocatalysts such as $[(C_6H_{13})_4N]_3\{PO\text{-}[W(O)(O_2)_2]_4\}$,[56b] Ti-Al-MCM-22, and Ti-MCM-22.[56c]

Scheme 27

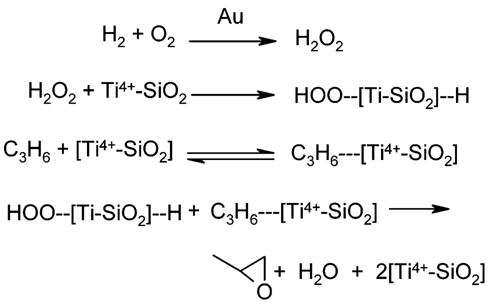


2.10. Gold Catalysts

Gold has long been thought to be chemically inert; however, it has recently been proven that its catalytic performance is dramatically tunable by control of the particle size and by careful selection of the support metal oxide. A typical example is the selective oxidation of propene in a gas containing oxygen and hydrogen.[57,58] When gold is deposited (deposition−precipitation method) on TiO$_2$, TiO$_2$/SiO$_2$, TS-1, TS-2, Ti-β, Ti-MCM-41, and Ti-MCM-48 as a highly dispersed nanosize hemispherical particle with a diameter of 2.0−4.0 nm, it produces propene oxide with selectivities >90% and conversions up to 9.8% at temperatures of 30−160 °C. The oxidation of hydrogen to form water is depressed by propene, whereas propene oxidation is not only enhanced but also restricted to partial oxidation by hydrogen. The reaction rate is almost independent of the concentration of propene and increases linearly with increasing concentrations of oxygen and hydrogen, and a hydroperoxide-like intermediate is proposed for this epoxidation (Scheme 28).

Modification of the Au/TiO$_2$/SiO$_2$ catalysts with platinum is beneficial for both the activity and selectivity in the propene epoxidation.[59] The water−propene oxide ratio decreases upon the addition of platinum to the Au/TiO$_2$/SiO$_2$ catalyst, whereas the epoxidation activity is maintained. Hydrogenation of propene to unwanted propane does not occur at temperatures below 100 °C.

Scheme 28



3. Alkenes to Alcohols and Ketones

Alcohols and ketones are important compounds in synthetic and industrial chemistry.[7e] Studies are focused on the preparation of these compounds from alkenes by an oxidation process using molecular oxygen (eq 1). These reactions are different from the

$$RCH{=}CH_2 \xrightarrow{M/O_2} RCOMe/RCHOHCH_2OH/RCHOHCH_3 \quad (M = Mn, Co, Rh, Os) \quad (1)$$

classical Wacker oxidation, as they do not involve any redox coreductants. This section covers the transition metal catalyzed oxidation of alkenes to alcohols and ketones with molecular oxygen.

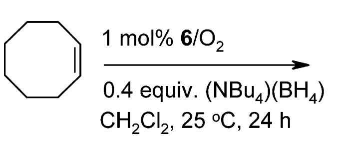
3.1. Manganese Catalysts

The oxidation of unfunctionalized alkenes to the corresponding alcohols has been reported using manganese complex **6** and molecular oxygen in the presence of $NaBH_4$ and $[NBu_4]BH_4$ (Scheme 29).[60] In these reactions the actual product is a ketone, which undergoes reduction in situ to an alcohol by an excess of borohydride. Mukaiyama and co-workers described the hydration of α,β-unsaturated esters to α-hydroxy esters using $Mn(dpm)_2$ and molecular oxygen in the presence of phenylsilane in 2-propanol.[61] This reaction provides an effective route for the direct hydration of α,β-unsaturated esters (Scheme 30).

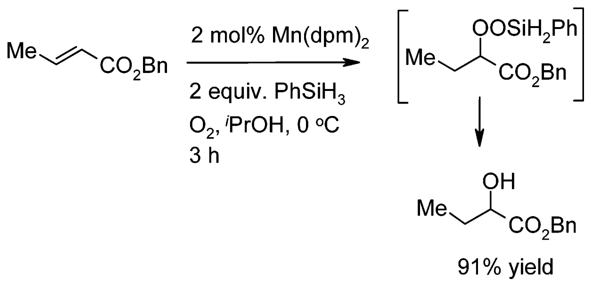
3.2. Cobalt Catalysts

Cobalt(II) complexes have been studied for the oxidation of alkenes to alcohols and ketones with molecular oxygen. Drago and co-workers reported the oxidation of styrene and 1-hexene using Co(SMDPT) **37** [SMDPT = (3-(salicylidieneimino)propyl)methylaminato] in the presence of 2−6 atm of molecular oxygen in ethanol at 20−80 °C (Scheme 31).[62,63] Only terminal alkenes are found to be reactive in this catalytic system. The reaction occurs in ethanol or methanol but not in *tert*-butyl or isopropyl alcohol. The alcohol is concomitantly oxidized during the reaction and may act as a coreducing agent and/or favor the formation of cobalt hydride. The ratio of the hydrated product to the oxidized product is influenced by the concentration of ethanol, although the ketone is produced as the major product in all cases. Hydroperoxide has been proposed as a key intermediate for this system (Scheme 32).

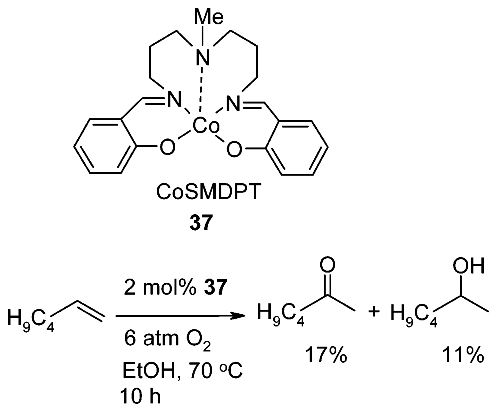
Scheme 29



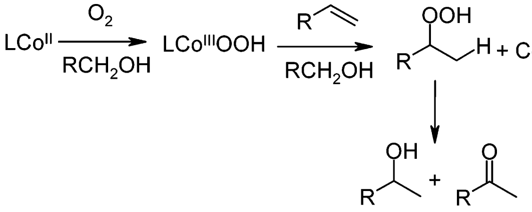
Scheme 30



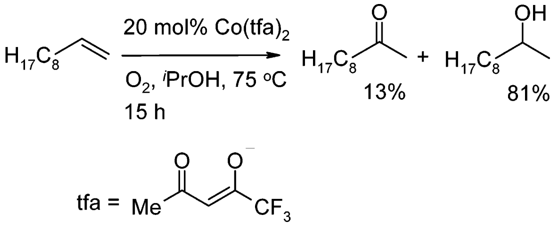
Scheme 31



Scheme 32

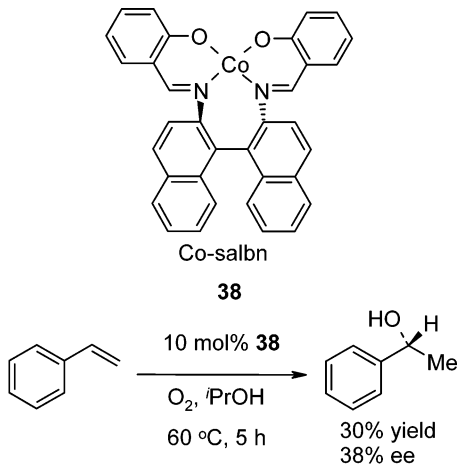


Scheme 33

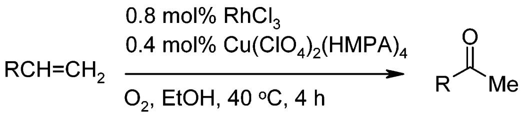


Cobalt(II)−β-diketone complexes having electron-withdrawing groups have been studied for the aerobic hydration of alkenes (Scheme 33).[64] Addition of molecular sieves or azeotropic removal of water increases the yield of the desired alcohol significantly. Because the conventional method of hydration of alkenes is performed under strongly acidic conditions, functionalized alkenes having ester, amide, or acetal groups cannot be usually employed,[65] whereas even alkenes containing an acetal group can be hydrated to give the desired product in high yield using the cobalt(II)-catalyzed systems because of their neutral conditions. Nishinaga and co-workers reported the enantioselective aerobic hydration of styrene to phen-

Scheme 34



Scheme 35



R-Group	Selectivity (%)	TON
$^nC_4H_9$-	98	60
$^nC_6H_{13}$-	98	52
$^nC_{10}H_{21}$-	98	40
$^iC_4H_9$-	98	30
C_6H_5-	97	30

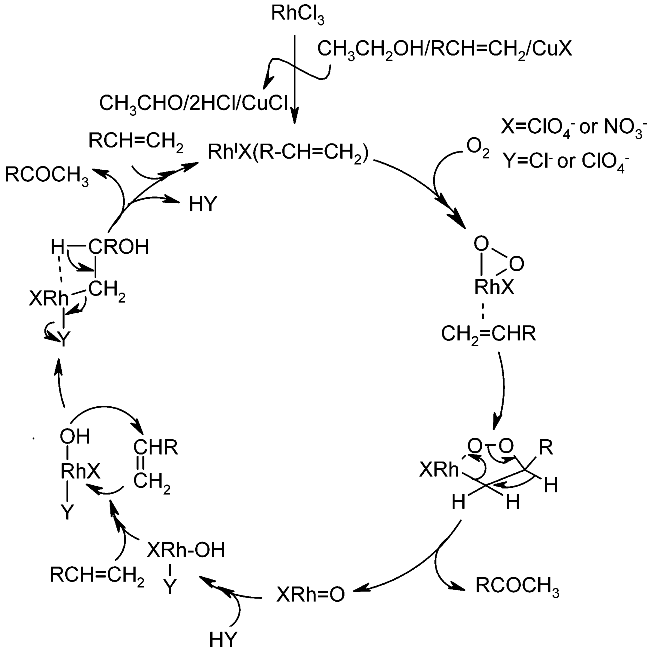
ylethanol in 38% ee using chiral *R*-Co–salen **38** in 2-propanol (Scheme 34).[66,67]

3.3. Rhodium Catalysts

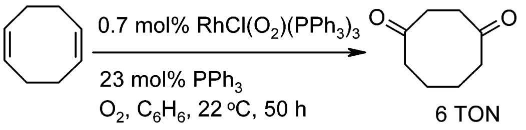
Rhodium complexes are found to be effective catalysts for the selective oxidation of terminal alkenes to methyl ketones with molecular oxygen.[68,69] Among the several catalytic systems investigated, the combination of $RhCl_3$ and $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ is more effective, and several substrates have been oxidized to the corresponding methyl ketones in ethanol at ambient temperature (Scheme 35).[69b] Both oxygen atoms are incorporated into 2 mol of alkene to give 2 mol of ketone with selectivity up to 98%, based on the consumed alkene and molecular oxygen (Scheme 36). The mechanism of this reaction is different from the conventional Wacker chemistry as, in this system, water is not involved as the oxygen source. In fact, it is an inhibitor, and the presence of a dehydrating agent such as 2,2-dimethoxypropane speeds the reaction. This clearly suggests that molecular oxygen is the source of the oxygen atom present in the formed ketone, and the classical Wacker type mechanism is not operative under these conditions.

The rhodium–molecular oxygen complex $RhCl(O_2)(PPh_3)_2$ transfers both oxygen atoms to 1 mol of coordinated 1,5-cyclooctadiene to give cyclooctane-1,4-dione, without the intermediate formation of monoketone (Scheme 37).[70] In the presence of excess of PPh_3, the reaction becomes slightly catalytic.

Scheme 36



Scheme 37



Scheme 38

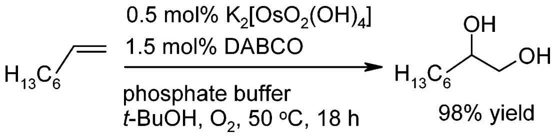


Table 5. Osmium-Catalyzed Dihydroxylation of Alkenes with Molecular Oxygen[a]

entry	substrate	conversion (%)	selectivity (%)	yield (%)	ee (%)
1	vinylnaphthalene	72	76	55	96 (*R*)
2	styrene	67	78	52	90 (*R*)
3	α-methylstyrene	100	96	96	80 (*R*)
4	1-phenylcyclohexene	53	96	51	86 (*R*)
5	1-octene	99	98	98	65 (*R*)

[a] Substrate (2 mmol) was allowed to react in the presence of $K_2[OsO_2(OH)_4]$ (0.5–2 mol %) and $(DHQD)_2PHAL$ (DHQD-PHAL = hydroquinidine 1,4-phthalazinediyl diether; 1.5–6 mol %) in a mixture of aqueous buffer solution (25 mL, pH 10.4) and *t*-BuOH (10 mL) at 1 atm of molecular oxygen and 50 °C with stirring for 16–24 h.

3.4. Osmium Catalysts

Osmium-catalyzed dihydroxylation of alkenes is reported with molecular oxygen at normal pressure in a basic two-phase system.[71] Both oxygen atoms are incorporated into the product in an atom-efficient manner. The diols are obtained in high yields, and the catalyst can be recycled (Scheme 38). Importantly, the use of chiral quinine and quinidine ligands leads to asymmetric dihydroxylation with good enantioselectivity (Table 5).

4. Wacker Oxidation

The oxidation of alkenes based on palladium complexes has evolved into highly useful methodologies in organic synthesis (eq 2). The Wacker–Hoechst

$$CH_2{=}CH_2 + O_2 \xrightarrow[CuCl_2 \atop H_2O]{PdCl_2} CH_3CHO \qquad (2)$$

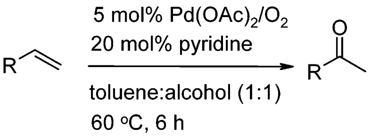
acetaldehyde process, the oxidation of propene to acetone, the acetoxylation of ethene to vinyl acetate and that of propene to allyl acetate, and the diacetoxylation of butadiene to 1,4-diacetoxy-2-butene are important commercial processes. A number of books and review articles have been published on these systems.[7e,72,73] The following section reviews the progress achieved on the Wacker type of oxidation using different catalytic systems.

4.1. Oxidation to Ketones

The oxidation of terminal alkenes by the Wacker system consisting of $PdCl_2/CuCl_2$ with molecular oxygen to methyl ketones is a well-established and important process in both synthetic and industrial chemistry. However, it has some disadvantages caused by the chlorine anion, which leads to the formation of chlorinated byproducts and corrodes the reactor, and is not suitable for the oxidation of higher alkenes. To overcome such drawbacks, much attention has been focused on developing halide-free catalytic systems.

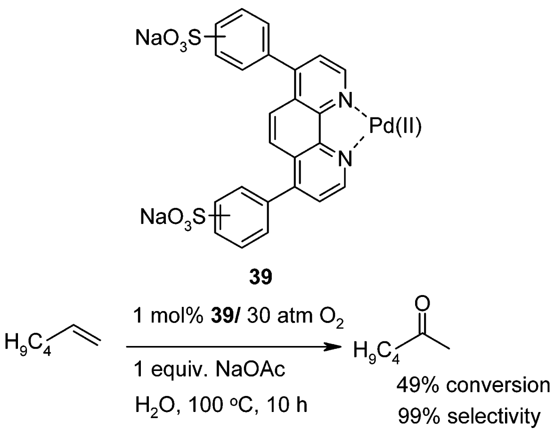
$Pd(OAc)_2$ has been used in combination with polyaniline[74a] and pyridine/2-propanol[74b] for the oxidation of terminal alkenes to methyl ketones in the presence of molecular oxygen (Scheme 39). Methanol, ethanol, and 2-butanol have also been employed as coreductants, but they are less effective, affording the ketones in <26% yield.[74b] Sheldon and co-workers studied the water-soluble palladium(II) complex **39** for the oxidation of alkenes in a biphase system at 100 °C.[75] The terminal alkenes are oxidized to the corresponding methyl ketones in 48–50% conversion and 100% selectivity (Scheme 40). In the case of cyclic alkenes such as cyclooctene the oxidation leads to cyclooctanone (100% selectivity), whereas cyclohexene and cyclopentene give a mixture of compounds (~50%) due to allylic oxidation. The addition of sodium acetate is necessary for this system to prevent the formation of inactive dimers, giant palladium clusters or even colloidal palladium. To rationalize these results, a mechanism is proposed as shown in Scheme 41. In the first step a palladium dimer with two bridging hydroxy ligands is dissociated via coordination of the alkene. This is followed by intramolecular attack of hydroxide on the coordinated alkene. The resulting β-hydroxyalkyl–palladium complex decomposes into 2-alkanone and a zero-valent palladium species. The latter is reoxidized with molecular oxygen, giving palladium peroxide, which on coupling with 1 equiv of zero-valent palladium regenerates the starting palladium dimer.

Scheme 39

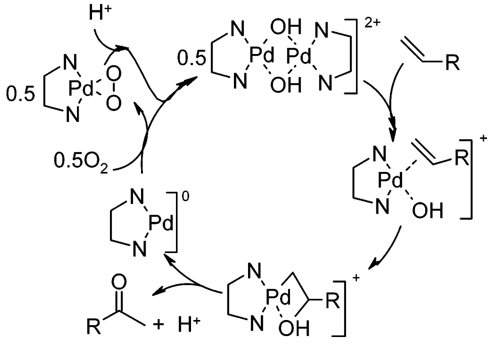


R-Group	Yield (%)
$^nC_{10}H_{21}$	72
$^nC_6H_{13}$	80
$^nC_{12}H_{25}$	72
$OHCH_2(CH_2)_2$	21
$TBSOCH_2(CH_2)_2$	71
$BzOCH_2(CH_2)_2$	56
$THPOCH_2(CH_2)_2$	78
$OHCH_2(CH_2)_8$	71

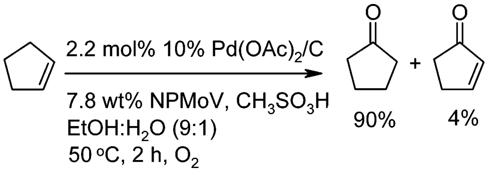
Scheme 40



Scheme 41

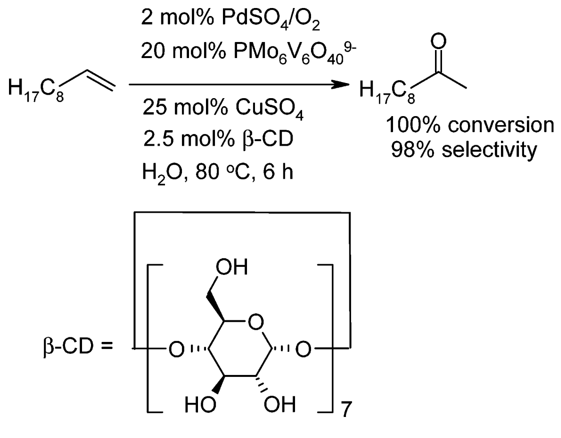


Scheme 42



Few studies have focused on the combined use of palladium(II) salts and polyoxometalates. Ishii and co-workers reported that $Pd(OAc)_2$ in combination with NPMoV/hydroquinone[76a] and NPMoV/C[76b] catalyzes efficiently the oxidation of series alkenes to the corresponding ketones in high yields (Scheme 42). The supported catalyst is recyclable without loss of activity. Monflier and co-workers carried out a biphase oxidation of 1-decene to 2-decanone in 98% yield (Scheme 43).[76c,d] In this case, a three-component catalytic system, $PdSO_4$, $PMo_6V_6O_{40}{}^{9-}$, and $CuSO_4$, is used, where Cu(II) is suggested to promote the palladium reoxidation. The key point about this is the use of a β-cyclodextrin (β-CD) as a phase-transfer catalyst, which transfers 1-decene to the aqueous phase by a host–guest interaction. The catalytic system composed of $PdCl_2$, $H_5PV_2Mo_{10}O_{40}$, and KCl

Scheme 43



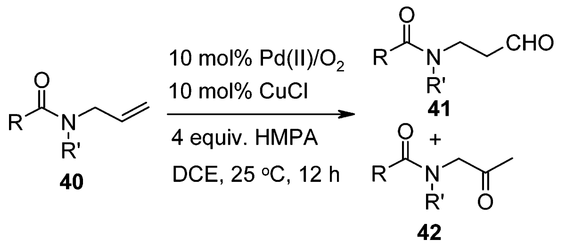
catalyzes the oxidation of propene to acetone in 89% conversion in poly(ethylene glycol).[76e]

Palladium salts supported on TiO_2 have been used for the oxidation of terminal alkenes.[77] Thus, by a combined use of $PdSO_4$, V_2O_5, and TiO_2, the oxidation of 1-butene to 2-butanone is reported at 49−120 °C in a continuous fixed-bed stainless steel reactor.[77a] The composition of this catalyst appears to be of major influence on its performance. Although the selectivity of 2-butanone is high (83%), its yield decreases rapidly from 23 to 9% due to loss of the activity of the catalyst (~60% in the first 100 h of operation), whereas the Pd-nanocluster supported on TiO_2 catalyzes the oxidation of a series of alkenes in the presence of $CuCl_2$.[77b] 1-Decene, 1-hexene, 1-octene, 1-dodecene, vinylcyclohexene, and *n*-butyl vinyl ether have been converted to the corresponding methyl ketones in 87−94% yield.

4.2. Oxidation to Aldehydes

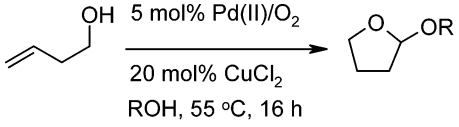
The Wacker-type oxidation is very efficient in oxidizing alkenes to the corresponding aldehydes. Thus, the oxidation of *N*-allyl-*N*-methylbenzamides **40** to aldehydes **41** and ketones **42** is reported using the catalytic system composed of $(MeCN)_2PdCl_2/CuCl$ and HMPA under anhydrous conditions with molecular oxygen (Scheme 44).[78a] In the case of 1,5-dienes, one of the double bonds can be selectively converted to aldehyde without affecting the other double bond to afford the corresponding olefinic aldehyde in the presence of $PdCl_2/CuCl$ in $DMF-H_2O$.[78b] Feringa studied the Wacker oxidation of terminal alkenes to aldehydes using $(MeCN)_2PdClNO_2/CuCl_2$ in *t*-BuOH, whereas homoallylic alcohols are transformed into the corresponding cyclic acetals in high yields (Scheme 45).[79]

Scheme 44



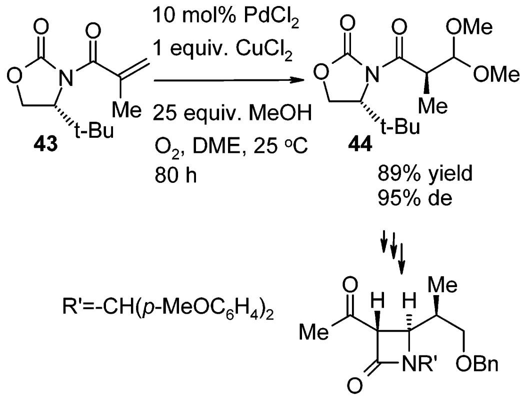
R	R'	Yield (%) (41:42)
Ph	Me	52 (9:1)
Me	Ph	71 (3:1)
Me	Me	68 (9:1)
-$[CH_2]_5$-		62 (9:1)

Scheme 45



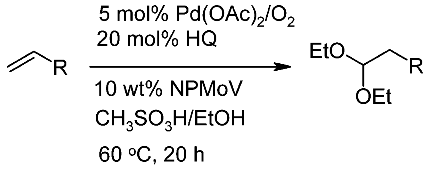
R-Group	Yield (%)
^{i}Pr	26
^{t}Bu	94

Scheme 46



45

Scheme 47



R-Group	Yield (%)
CHO	38
CN	99
CO_2Et	99
$CH(OEt)_2$	58

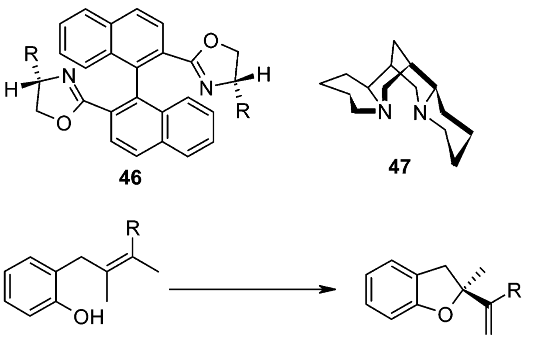
4.3. Acetal Formation

Murahashi and co-workers reported the asymmetric acetal formation from methacrylamide **43** using $PdCl_2/CuCl$ in methanol under oxygen atmosphere (Scheme 46).[80] This reaction proceeds with high chemoselectivity and 95% diastereomeric excess. Reductive cleavage of the auxiliary yields acetal **44**, which has been used in the synthesis of an α,β-methylcarbapenem **45**. This route provides an alternative to the enzymatic synthesis of (*S*)-3-hydroxy-2-methylpropanoic acid. The catalytic system composed of NPMoV and hydroquinone (HQ) catalyzes the acetal formation of monosubstituted alkenes in acetic acid, whereas cyclic alkenes undergo allylic oxidation to give the corresponding allylic acetates in high yield (Scheme 47).[76a]

4.4. Intramolecular Alkoxypalladation

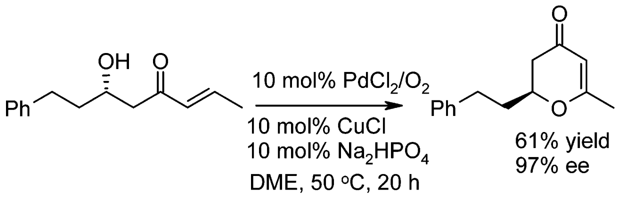
Intramolecular alkoxypalladation is another Wacker type of reaction, which gives rise to the synthesis

Scheme 48



Reaction Conditions	R-Group	Yield (%)	ee (%)	Ref.
10 mol% $Pd(TFA)_2$, 10 mol% **46**, 4 equiv. BQ, O_2, MeOH, 60 °C, 24 h.	Me	72	97	81f
10 mol% $Pd(TFA)_2$, 100 mol% **47**, 2 equiv. $Ca(OH)_2$, MS 3A, O_2, Toluene, 80 °C, 36 h.	H	87	81	81g

Scheme 49



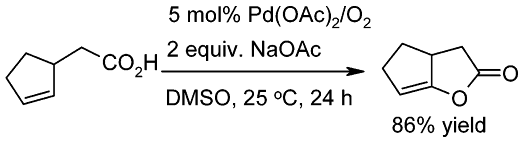
of cyclic ethers.[81] Following the Murahashi synthesis of tetrahydrofurans by oxidative cyclization of γ,δ-unsaturated alcohols with molecular oxygen using $Pd(OAc)_2$ and $Cu(OAc)_2$,[81a] intramolecular oxidative cyclization of aliphatic alcohols,[81c-e] phenols,[81b,f,g] and β-hydroxyenones[81h] is reported. The cyclization of *o*-allylphenols is performed using $Pd(TFA)_2$ in the presence of 1,4-benzoquinone (BQ)[81f] or $Ca(OH)_2$.[81g] In the presence of chiral bis-oxazolyl-1,1-binaphthyl ligand[81f] **46** or (−)-sparteine[81g] **47**, the corresponding cyclic ethers are formed in high enantioselectivity (Scheme 48). The cyclization of β-hydroxyenones is reported by the combined use of $PdCl_2$, CuCl, and Na_2HPO_4.[81h] This system can be used for the transformation of enantiopure β-hydroxyenone to 2,3-dihydro-4*H*-pyran-4-one without loss of the optical purity (Scheme 49).

4.5. Acetoxylation and Related Reactions

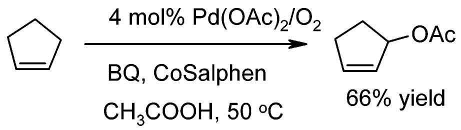
Palladium-catalyzed acetoxylation of alkenes using acetic acid is a successful commercial process.[82] Larock and Hightower studied the intramolecular cyclization of alkenoic acid to the corresponding lactone in high yield using $Pd(OAc)_2$ in DMSO in the presence of molecular oxygen (Scheme 50).[83]

Backvall and co-workers explored the oxidation of cyclic alkenes using a catalytic system consisting of $Pd(OAc)_2$, quinone, and Co−salophen in the presence of molecular oxygen.[84] In particular, five-, six- and seven-membered cyclic alkenes are oxidized to the corresponding allylic carboxylates.[85] Cyclohexene is quantitatively oxidized to 1-acetoxy-2-cyclohexene in only 2 h in acetic acid at 60 °C. Other oxygen-activating catalysts such as heteropolyacid[86] and metal−macrocycles[84,85] can be employed for this transformation in the place of Co−salophen (Scheme 51).

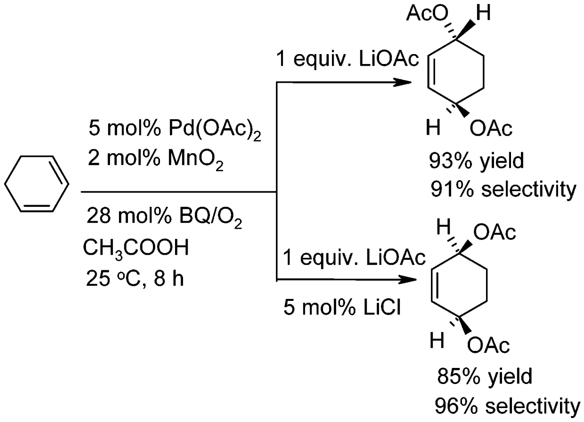
Scheme 50



Scheme 51



Scheme 52



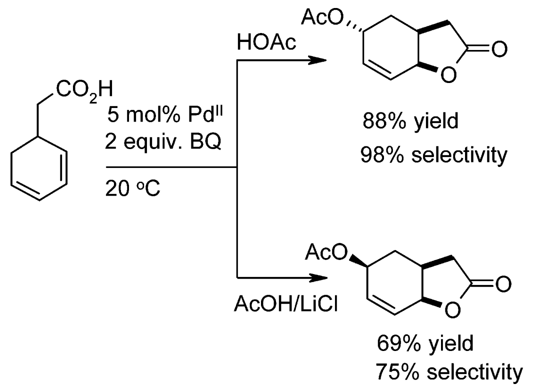
Several studies have focused on the regio- and stereoselective palladium-catalyzed 1,4-oxidation of conjugated dienes to 1,4-diacetates.[87] These reactions proceed at room temperature in acetic acid in the presence of a lithium carboxylate and benzoquinone, and the conditions are milder than those required for the acetylation of monoalkenes (Scheme 52).

Intramolecular versions of the 1,4-oxidations have been developed.[88,89] Backvall and co-workers have elegantly demonstrated an intramolecular cyclization of cyclohexadiene acetic acid to the corresponding *cis*-fused γ-lactone. This reaction occurs via intramolecular nucleophilic attack by the carboxylic group in a highly regio- and stereoselective manner, leading to a cis-fused heterocycle. The lactone formation is occurring by a successive intramolecular and intermolecular nucleophilic attack. In the first instance, the carboxylate attacks intramolecularly to the diene complexed with palladium in an anti fashion. This cyclization subsequently leads to a π-allyl palladium complex, which is attacked intermolecularly by acetic acid, leading to the observed stereochemistry. The intermolecular attack by acetic acid has been elegantly controlled by manipulation of the reaction conditions, which lead to a *syn* or *anti* lactone (Scheme 53).

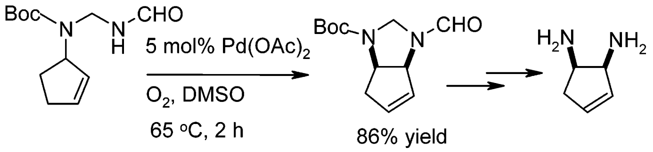
4.6. Aminopalladation

In a π-allyl palladium complex, the addition of amines often results in the displacement of the alkene from the palladium complex.[7e] This problem

Scheme 53



Scheme 54



has been circumvented by using amides, carbomates, and urea.[90] Thus, intramolecular aminopalladation or Pd-mediated aminocarbonylation of alkenes and allenes has widely employed the amide as a source of nitrogen in the synthesis of nitrogen-containing five- and six-membered heterocycles.[91] The Pd(II)-catalyzed 5-exo cyclization of aminals in DMSO with molecular oxygen is illustrative, and it is found that formamides are superior nucleophiles to free amines in these oxidations (Scheme 54).[92]

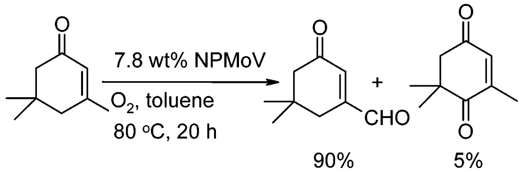
5. Allylic Oxidation

Allylic oxidation of alkenes is a fundamental and important functional transformation in synthetic chemistry.[93] Many studies are focused on the allylic oxidation of alkenes with transition metal catalysts.[7f] This section covers the various catalytic systems employed for the allylic oxidation of alkenes with molecular oxygen and transition metal catalysts. The reactions with palladium catalysts are incorporated in the Wacker-type oxidation.

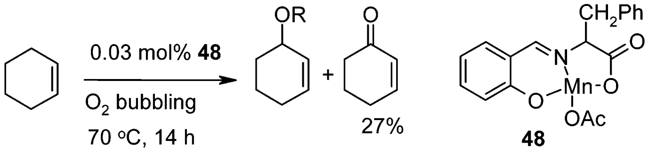
5.1. Vanadium and Molybdenum Catalysts

Ishii and co-workers reported the allylic oxidation of isophorone using polyoxometalates, NPMoV and NPMoV/S (S = C, SiO_2, or Al_2O_3), in the presence of molecular oxygen (Scheme 55).[94] The best performance available is a 15:1 mixture of 3-formyl-5,5-dimethyl-2-cyclohexen-1-one and keto-isophorone with 81% yield in the presence of NPMoV/C. This result is particularly important because the conventional oxidations usually provide the regioisomer, keto-isophorone.[95] The pore size of the supports appears to be an important factor governing the regioselectivity in these reactions.

Scheme 55

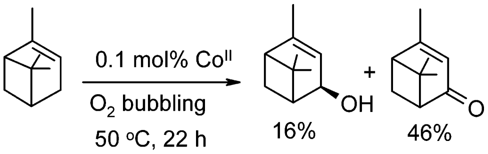


Scheme 56

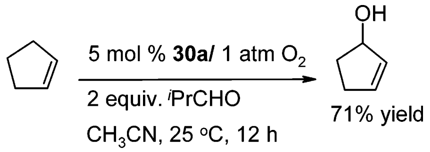


R-Group	Yield (%)
H	15
OH	32

Scheme 57



Scheme 58



5.2. Manganese Catalysts

The chiral manganese Schiff base complex **48** has been shown to catalyze the oxidation of cyclohexene into a mixture of cyclohexenol, cyclohexenone, and cyclohexenyl hydroperoxide without a coreductant under oxygen atmosphere (Scheme 56).[96] The influence of reaction temperature and additive on the product distribution has been studied.

5.3. Cobalt Catalysts

Cobalt catalysts have been studied for the allylic oxidation of alkenes in the presence as well as absence of coreductants. Lajunen and co-workers carried out the oxidation of neat α-pinene using Co(4-methylpyridine)$_2$Br$_2$ at 50 °C in 10% glacial acetic acid under a flow of oxygen where *trans*-verbenol (16%) and verbenone (46%) are obtained as the major compounds along with a trace of epoxide (Scheme 57).[97] The zeolite-Y-supported Co−salophen **49** (**49**−Y) catalyzes regioselectively (100%) the oxidation of isophorone to 3-formyl-5,5-dimethyl-2-cyclohexen-1-one in quantitative yield at ambient conditions.[98] The catalytic activity and selectivity of the encapsulated catalyst **49**−Y are significantly higher than those of its homogeneous analogue **49**. Iqbal and co-workers reported the allylic oxidation of cyclic alkenes with **30a** in the presence of 2-methylpropanal and atmospheric oxygen (Scheme 58).[99] By this method, cyclopentene can be oxidized to cyclopentenol in 71% yield, whereas cyclohexene, cycloheptene, and carene provide a mixture of the corresponding enols and enones in good yields.

6. Oxidative Dehydrogenation of Alkanes to Alkenes

Oxidative dehydrogenation (ODH) of light alkanes (C_2−C_6) in a flow of oxygen for the production of

Table 6. ODH of Alkanes Catalyzed by Vanadium-Based Catalysts with Molecular Oxygen[a]

entry	substrate	catalyst	temperature (°C)	conversion (%)	selectivity (%)	product(s)	ref
1	C_2H_6	V_2O_5	923	10.4	93	C_2H_4	100
		V_2O_5/MgO	773	10.2	52		101
		MoVNbO	400	21.5	60.5		102
		NiVO/VSbO	500	16.5	32.3		103
		VCoAPO-18	600	41.3	62.1		104
		$VOPO_4/TiO_2$	550	10	60		105
		$FeVOP/Al_2O_3$	550	14.6	82		106
2	C_3H_8	V_2O_5	813	22.6	28	C_3H_6	100
		$V_2O_5/\tilde{\gamma}$-Al_2O_3	504	17.5	34		107
		V/MgO	585	50	30		108
		VMgTi	500	10	85		110
		VWO/γ-Al_2O_3	400	45	60		111a
		V/MgO	500	82	64		112
3	$^nC_4H_{10}$	V-MCM-4	550	13.7	57.3	$^nC_4H_8{}^nC_4H_6$	113
		$Mg_{0.72}V_{0.26}Cr_{0.01}Ti_{0.01}O_x$	540	42	63.5		115
		$Mg_{0\cdot58}V_{0\cdot32}Mo_{0\cdot10}O_x$	540	16.9	62.5		116
		$NdVO_4$	700	12.5	55.9		117
4	$^iC_4H_{10}$	V/MgO	550	48.6	70.2		118
		$V_2O_5/TiO_2/SiO_2$	515	16.4	19.4		119
		V-MCM-41	550	10	52		120
5	$^nC_5H_{12}$	V/MgO	500	27.9	100	$^nC_5H_8$	121
6	vinylcyclohexene	$PV_5Mo_{10}O_{40}{}^{5-}/C$	220	60	40	styrene	122

[a] Carried out under air or O_2.

Table 7. ODH of Alkanes Catalyzed by Molybdenum-Based Catalysts with Molecular Oxygen[a]

entry	substrate	catalyst	temperature (°C)	conversion (%)	selectivity (%)	product	ref
1	C_2H_6	Mo/Si/Ti	600	39.2	44.1	C_2H_4	124
2	C_3H_8	$Ni_{0.5}Co_{0.5}MoO_4$	560	15	71.5	C_3H_6	123
		$Ni_{0.5}Co_{0.5}MoO_4/SiO_2$	560	34	47		123
		Mo−HTC	600	21	100		125
3	$^nC_4H_{10}$	$NiMoO_4$	525	4	60	$^nC_4H_8$	126
		$MNiMoO_4$ (M = Ca, Sr, or Ba)	525	4	70	$^nC_4H_6$	126
4	$^iC_4H_{10}$	$NiMoO_4/SiO_2$	475	29.2	15	$^iC_4H_8$	127
5	ethylbenzene	$Fe_2BiMo_2Al_{0.25}O_x$	653	100	97.7	styrene	128

[a] Carried out under air or O_2.

short-chain alkenes is one of the novel routes currently proposed for the exploitation of natural gas as a raw material for highly priced and clean chemicals (eq 3). It is exothermal and takes place at lower

$$C_nH_{2n+2}\xrightarrow[\Delta]{M/O_2}C_nH_{2n} + H_2O \qquad (3)$$

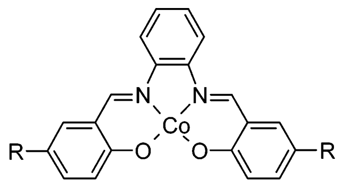
temperature than the conventional dehydrogenation process. Also, the amount of heat released and the presence of oxygen in the ODH limits coke deposition, thus preventing a loss of catalytic activity. However, the key point of the ODH is the development of catalysts capable of activating only the C−H bonds of alkanes to alkenes in the presence of oxygen. The selectivity of the ODH products depends on the specific alkane fed, on the metal content of the catalysts, and on the nature of the matrix and/or support in which metal atoms are incorporated.[100] The following section reviews the recent progress of this reaction catalyzed by transition metal salts.

6.1. Vanadium and Molybdenum Catalysts

The large majority of the catalysts studied for the ODH of lighter alkanes are based on the chemistry of vanadium oxides.[100−122] Their catalytic behavior is usually modified when deposited on SiO_2, Al_2O_3, TiO_2, and MgO with new surface structure.[101−121] The most profound changes are frequently observed at low vanadium loading, not exceeding a monolayer, and species in the monolayer display higher catalytic activity and/or selectivity than the bulk V_2O_5. The ODH of C_2−C_5 alkanes and vinylcyclohexene are reported with 10−60% conversion and 52−100% selectivity (Table 6).[102,103,119−122]

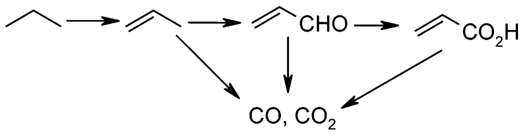
Molybdenum-based catalysts have been studied for the ODH of C_2−C_4 alkanes[123−127] and ethylbenzene[128] (Table 7). A recent comprehensive study of propane ODH over SiO_2-supported molybdate-based catalysts of the formula $NMoO_4$ (N = Ni, Co, Mg, Mn, and Zn) reports a maximum conversion of 34% (47% selectivity) with $Ni_{0.5}Co_{0.5}MoO_4/SiO_2$.[123] As compared to the ODH catalysts, which give rise to alkenes, the Ni−Co−molybdate catalyzes a complete oxidation of the initial propene to CO and CO_2 under different reaction conditions (Scheme 59). The ODH of C_2−C_4 alkanes has shown 4−39% conversion and 15−72% selectivity,[123,125−127] whereas ethylbenzene is converted to styrene with 98% yield.[128]

Scheme 59



R= H, Cl, Br, NO_2

49



6.2. Chromium Catalysts

Few studies have focused on the ODH of C_2-C_4 alkanes using chromium oxide (Cr_2O_3) supported on Al_2O_3, SiO_2, TiO_2, and ZrO_2.[129,130] The ODH of C_3-C_4 alkanes has shown 21% conversion and 45% selectivity, whereas ethane is converted to ethene in 20% conversion and 6% selectivity.

6.3. Manganese Catalysts

Au and co-workers reported that the halide-doped perovskite-type oxides, $AMn_{1-x}Cu_xO_{3-}\delta X\sigma$ ($A = La_{0.8}Ba_{0.2}$; X = F or Cl), catalyze the ODH of ethane with up to 73% conversion and 69.5% selectivity in the presence of molecular oxygen.[131] The addition of halide ions to the perovskites reduces deep ethene oxidation. X-ray powder diffraction results indicate that at $x = 0.3$ the halide-doped $AMn_{1-x}Cu_xO_{3-}\delta X\sigma$ (X = F or Cl) products are single-phase and cubic in structure. However, when the x value exceeds 0.7, there are trace amounts of La_2CuO_4 and/or CuO phases besides the perovskite phase. Similarly, the alumina-supported mixed metal oxide, $LaMnO_3/\gamma Al_2O_3$, has been shown to catalyze the ODH of ethane with 84% conversion and 65% selectivity in the presence of molecular oxygen.[132]

6.4. Iron Catalysts

Iron phosphate phases [$FePO_4$, $Fe_2P_2O_7$, α-$Fe_3(P_2O_7)_2$, and β-$Fe_3(P_2O_7)_2$] have been studied for the ODH of ethane at temperatures ranging from 400 to 675 °C.[133a] The catalyst with a P/Fe ratio of 1.2:1 is found to more efficiently catalyze the ODH of ethane, with 42% conversion and 84% selectivity under atmospheric pressure.

6.5. Ruthenium Catalysts

Alumina-supported ruthenium hydroxides, $Ru(OH)_x/Al_2O_3$, have been studied for the ODH of a series of alkylbenzenes with quantitative yields under molecular oxygen.[133b] The recovered catalyst is reusable without loss of activity.

6.6. Cobalt Catalysts

Cobalt−titania (Co/TiO_2)[134,135] and cobalt−zeolite (CoH−BEA−zeolite)[136] catalysts of different cobalt content prepared by impregnation have been studied for the ODH of C_2-C_3 alkanes. The best conversions available are 28% (67% selectivity) for ethane to ethene and 8% (41% selectivity) for propane to propene, respectively.

6.7. Nickel Catalysts

Nickel oxide (NiO) supported on ThO_2, CeO_2, MgO, Al_2O_3, and SiO_2 has been tested for the ODH of C_2-C_4 alkanes.[137−139] NiO dispersed on Al_2O_3 catalyzed the ODH of ethane with 59.1% conversion and 65.3% selectivity.[137] The catalytic system using Ce−Ni−O is found to be efficient for the ODH of C_3-C_4 alkanes, providing 10−19% conversion and 59−60% selectivity.[138,139]

6.8. Platinum Catalysts

Most of the data reported on the partial oxidation of light alkanes with platinum-based catalysts refer to low surface area Pt-coated Al_2O_3 foam monoliths.[140−142] Schmidt and co-workers reported very high yields of alkenes in the ODH of C_2-C_6 alkanes over Pt-coated α-Al_2O_3 foam monoliths operating adiabatically at short contact times (a few milliseconds) under atmospheric pressure and at 700−900 °C.[140a] In the cases of C_2-C_4 alkanes, almost complete conversion of the alkanes and selectivities to alkenes of >60% are reported. They have also demonstrated that platinum is the best catalyst compared to rhodium and palladium for the ODH of alkanes at very short contact times. They have found, for instance, that rhodium mainly produces CO/H_2 mixtures, whereas palladium rapidly undergoes deactivation due to coking. Flick and Huff compared the performance of a Pt/α-Al_2O_3 monolith with that of a much higher surface area in Pt/γ-Al_2O_3 pellets and found that the Pt/γ-Al_2O_3 catalyst is active in the ODH of ethane with 85% conversion (50% selectivity) under adiabatic operation at few-millisecond contact times.[141] Pt/Sn/γ-Al_2O_3 is investigated for the ODH of n-butane with 22% conversion (20% selectivity) at 450 °C under atmospheric pressure.[142]

7. Oxygenation of Alkanes

The conversion of alkanes to oxygen-containing compounds with molecular oxygen catalyzed by transition metals is one of the most important and fundamental transformations in industrial chemistry.[143,144] There have been a number of publications that have dealt with this problem, and this section surveys the recent studies of this reaction.

7.1. Vanadium and Molybdenum Catalysts

The oxidation of alkanes catalyzed by vanadium- and molybdenum-based catalysts can be divided into three groups: (i) VPO-catalyzed reactions; (ii) molybdenum-based mixed metal oxides (MMO) and polyoxometalates catalyzed reactions; and (iii) silica-supported vanadium- and molybdenum-catalyzed partial oxidations.

7.1.1. VPO Catalysts

For the selective oxidation of alkanes, there is one successful commercial example since 1970: n-butane

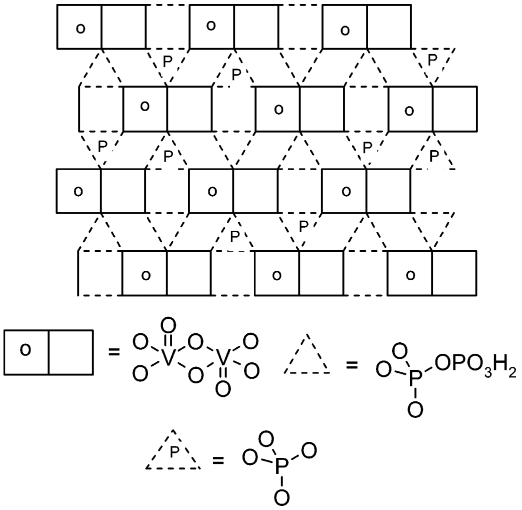
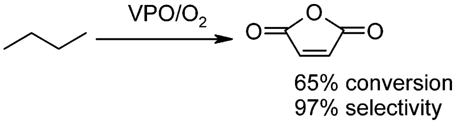


Figure 1.

Scheme 60



Scheme 61

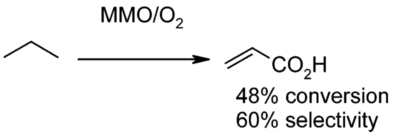


Table 8. Oxidation of Propane to Acrylic Acid Using VPO[a]

entry	catalyst	acrylic acid (%)	selectivity (%)	ref
1	$V_1P_{1.15}Te_{0.1-0.15}O$	10.5	30	149
2	$V_1P_{1.05}O$	14.4	39	150
3	$V_1P_{1.1}O$	14.7	32	151
4	VPO/TiO_2-SiO_2	13.3	61	152
5	$VPZr_{0.5}O$	14.8	81	153
6	Ce/VPO	18.8	68	154

[a] Carried out at 300−420 °C under air or O_2.

replacing benzene as the starting material to produce maleic anhydride over a VPO catalyst (Figure 1).[145] The reported yields of maleic anhydride vary from 45 to 67%, with *n*-butane conversion at ∼90% and selectivity to maleic anhydride ranging from 65% to as high as 97% (Scheme 60).[146,147] Although the performance varies somewhat depending on the catalyst preparation and modifiers, the VPO catalysts are very effective in *n*-butane oxidation as reflected by the high conversion and high selectivity to maleic anhydride.

The success of VPO catalysts in the *n*-butane oxidation has stimulated great interests in the selective oxidation of propane to acrylic acid (Scheme 61). Table 8 lists the composition and performance of various VPO type catalysts tested for the selective oxidation of propane to acrylic acid.[148−154] The composition Ce/VPO is more active and provides 18.8% of acrylic acid with 68% selectivity.[154] On the basis of the excellent performance of VPO for converting *n*-butane to maleic anhydride, it is reasonable to believe that they have real potential for converting propane to acrylic acid more effectively. The future of VPO catalysis research for propane oxidation needs to rely on a good understanding and systematic studies of the structural origin, such as active phases and active species. Once the active phases or active sites of the catalysts are identified, be they amorphous or crystal phases, it would be a challenging task to prepare the catalyst to increase its active site density.

Table 9. Oxidation of Propane to Acrylic Acid Using MMO[a]

entry	catalyst	acrylic acid (%)	selectivity (%)	ref
1	$Mo_1V_{0.4}Nb_{0.04}Bi_{0.08}Sb_{0.08}O_n$	6	29	155
2	$MoSnO_n$	2	48	156
3	$Mo_1Ni_1Te_{0.01}P_{0.02}O_n$	3	23	157
4	$Mo_1V_{0.03}Te_{0.23}Nb_{0.12}O_n$	48	60	158
5	$Mo_1V_{0.03}Sb_{0.16}Nb_{0.05}O_n$	16	32	159
6	$Mo_1V_{0.3}Sb_{0.25}N_{0.11}O_n$	12	61	160
7	$Mo_1V_{0.3}Sb_{0.23}Nb_{0.12}K_{0.13}O_n$	25	64	161
8	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	42	59	162
9	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	14	61	163

[a] Carried out at 360−420 °C under air or O_2.

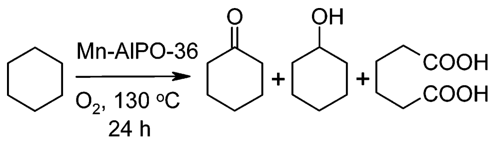
7.1.2. Mixed Metal Oxides and Polyoxometalates

Molybdenum-based mixed metal oxides[155−163] (MMOs) and polyoxometalates[164−169] have been studied for the oxidation of propane to acrylic acid. Although the history of the MMOs in propane to acrylic acid is relatively short, they have shown to date excellent conversion (80%) and selectivity (60%) (Table 9), whereas the actual yield of acrylic acid with polyoxometalates is relatively low (10.8% with 21.5% selectivity), but there is no follow-up for more than a decade on this important transformation.[166,167]

7.1.3. Silica-Supported Vanadium and Molybdenum Catalysts

Several studies are focused on the silica-supported vanadium- and molybdenum-catalyzed partial oxidation of alkanes.[170,171] Kobayashi and co-workers carried out the oxidations of ethane and propane to a mixture of acetaldehyde and acrolein in 2.8% conversion (62% selectivity) using $Cs/V/SiO_2$ (Cs/V/Si = 10:1:1000) at 400−600 °C.[170a] The presence of cesium in the catalyst increases the basicity and neutralizes the acid site of the catalyst. Fierro and co-workers reviewed the partial oxidation of methane with molecular oxygen.[171a] Many studies are focused on the oxidation of methane to methanol and formaldehyde over vanadium catalysts. V_2O_5/SiO_2 is widely investigated, and its catalytic activity and selectivity are related to the appearance of dispersed vanadium on the silica surface. The reaction is reported to proceed via a Mars−van Krevelen mechanism in which the lattice oxygen is incorporated in the formaldehyde, whereas the consumed oxygen is restored by molecular oxygen from the gas phase. Addition of NO in the feed increases the yield as well as the selectivity of the C_1-oxygenates. The best result available is 40% conversion and 40% selectivity in the presence of NO (0−2.92% vol) at 550 °C.[171b] This is the highest conversion so far available for the

Scheme 62



selectivity 47% 15% 33%
conversion 13% (233 TON)

oxidation of methane to methanol and formaldehyde at atmospheric pressure. It has been proposed that the NO gas alters the $CH_3^\bullet$ and $CH_3O_2^\bullet$ radical ratio and promotes the activation of methane.

Molybdenum-based catalysts have been widely investigated for the partial oxidation of methane with molecular oxygen.[171a] Most of the studies are focused on the molybdenum dispersed on silica, MoO_3/SiO_2, the catalytic activity and selectivity of which depend on both the Mo-loading and its preparation. This catalytic system has also shown that the oxygen incorporated in the formaldehyde is from the lattice molybdenum oxide and not from the gas phase molecular oxygen, and the role of molecular oxygen is to restore the oxidation state of the molybdenum (Mars−van Krevelen cycle). Zeolites, instead of silica, have been used as carriers to prepare molybdenum oxide catalysts for the methane oxidation. The resulting MoO_3/zeolite systems exhibited moderate activity and selectivity during the formaldehyde formation.

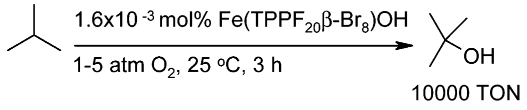
7.2. Manganese Catalysts

Manganese catalysts have been studied for the oxidation of cyclic alkanes. Thomas and co-workers reported the oxidation of cyclohexane into a mixture of cyclohexanol, cyclohexanone, and adipic acid using MnAlPO and air in high TON (Scheme 62),[172a−c] whereas the catalytic system with polyfluorinated manganese complex converts cyclooctane into a 5:3 mixture of cyclooctanone and cyclooctanol in 44946 TON under molecular oxgyen.[172d] The corresponding supported catalysts on SiO_2, polystyrene, and montmorillonite K10 are recyclable but less active (up to 10000 TON) compared to the homogeneous systems.

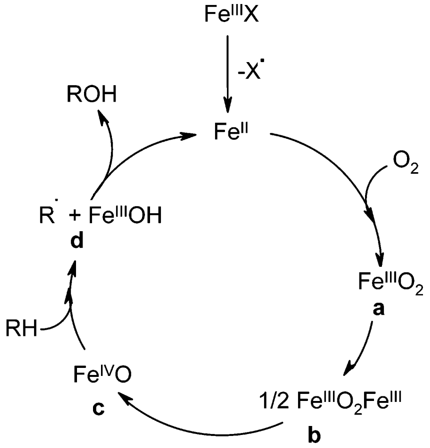
7.3. Iron Catalysts

Iron catalysts have been studied for the oxygenation of alkanes with a variety of ligands (Table 10).

Scheme 63



Scheme 64



Most of these studies are focused on the partial oxidation of alkanes to alcohols and ketones.

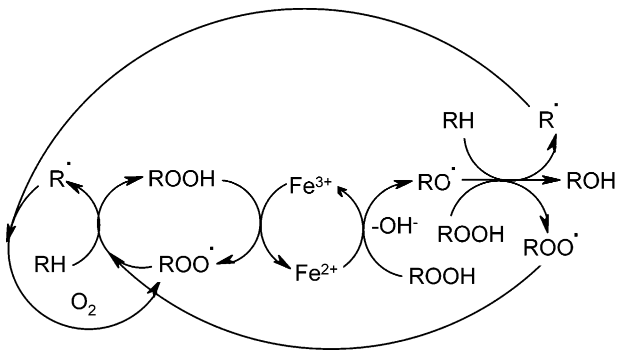
7.3.1. Reactions without Coreductants

Lyons and Ellis reported the oxidation of neat acyclic alkanes using iron−haloporphyrins under molecular oxygen (1−5 atm).[5b] Isobutane is oxidized to *tert*-butyl alcohol in 20000 TON in the presence of Fe(TPPF$_{20}\beta$-Br$_8$)OH [TPPF$_{20}\beta$-Br$_8$ = tetrakis(pentafluorophenyl β-octabromo)porphyrin] at 100 °C. Although in this reaction the catalyst decomposition is a problem at somewhat elevated temperatures (>60 °C), well over 10000 catalytic turnovers can be reached at ambient temperature with no decay of the catalyst (Scheme 63). Similarly, the oxidation of propane to a 1:1.1 mixture of isopropyl alcohol and acetone is reported with 541 TON in the presence of Fe(TPPF$_{20}\beta$-Br$_8$)N$_3$ at 125 °C. However, substituted alkanes such as 2-methylbutane, 3-methylpentane, 2,3-dimethylbutane, and 1,2,3-trimethylbutane are oxidized into a mixture of products due to oxidative cleavage of the carbon−carbon bond. The postulated mechanisms for these reactions are similar to those proposed for the biological oxidations by cytochrome P-450 and methanemonooxygenase (Scheme 64).[5b] Gray and co-workers studied the oxidation of

Table 10. Iron Complex Catalyzed Aerobic Partial Oxidation of Alkanes

entry	catalyst	alkane	products	coreductant	ref
1	Fe(TPPF$_{20}\beta$-Br$_8$)OH	isobutane	*t*-butanol	none	5b
2	Fe(TPPF$_{20}\beta$-Br$_8$)N$_3$	*n*-propane	2-propanol + acetone	none	5b
3	$[PW_9O_{37}][Fe_2Ni(OAc)_3]^{10-}$	adamantane	adamantanol + adamantanone	none	173
4	γ-SiW$_{10}$(Fe(OH$_2$))$_2$O$_{38}^{6-}$	cyclohexane	cyclohexanol + cyclohexanone	none	174
5	FeAlPO	cyclohexane	cyclohexanol + cyclohexanone + adipic acid	none	172a,b
6	$FeCl_3$	cyclohexane	cyclohexanol + cyclohexanone	H_2S	176
7	**50**	cyclohexane	cyclohexanol + cyclohexanone	H_2S	178
8	**50**	adamantane	adamantanol + adamantanone	H_2S	178
9	**51**	cyclohexane	cyclohexanol + cyclohexanone	PPh_3	178
10	Fe(TPFPP)Cl	cyclohexane	cyclohexanol + cyclohexanone	CH_3CHO	179
11	**52**	cyclohexane	cyclohexanol + cyclohexanone	CH_3CHO	180
12	Fe nanoparticles	cyclohexane	cyclohexanol + cyclohexanone	^{i}PrCHO	181a,b
13	Fe nanoparticles	adamantane	adamantanol + adamantanone	^{i}PrCHO	181a,b
14	**53**	cyclohexane	cyclohexanol + cyclohexanone	none	183

Scheme 65



3-methylpentane to 3-hydroxy-3-methylpentane (>99% selectivity) using iron–haloporphyrins and molecular oxygen in benzene at 60 °C.[5c] The product selectivity and radical trap experiment suggest that this reaction takes place by an autoxidation process (Scheme 65).

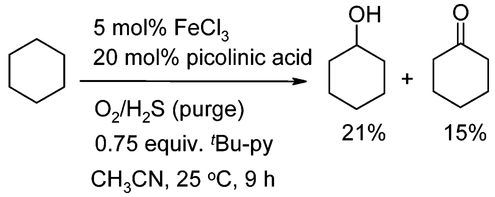
Few studies have focused on the use of iron-based polyoxometalates and aluminophosphates for the oxidation of cyclic alkanes. Mizuno and co-workers investigated the heteropolyoxometalates $[PW_9O_{37}][Fe_2Ni(OAc)_3]^{10-}$ and $\gamma\text{-}SiW_{10}(Fe(OH_2))_2O_{38}{}^{6-}$ for the oxidation of adamantane[173] and cyclohexane,[174] respectively. Both of the substrates are oxidized into a mixture of alcohol and ketone with up to 147 TON. Results obtained with the radical initiator and scavenger suggest that these reactions involve a radical pathway. Thomas and co-workers described the oxidation of cyclohexane to adipic acid with air in the presence of Fe–AlPO-31.[172a,b] This molecular sieve has narrow pores, with a 0.54-nm diameter. Cyclohexane is easily adsorbed in the micropores, but desorption of initial products such as cyclohexylperoxide or cyclohexanone is slow. Consequently, subsequent radical reactions occur until the cyclohexyl ring is broken to form linear products that are sufficiently mobile to diffuse out of the molecular sieve. In contrast, with a larger pore Fe–AlPO-5, cyclohexanol and cyclohexanone account for ~60% of the oxidation products. Thus, localization of a free radical reaction inside micropores seems to give rise to particular selectivities.

7.3.2. Reactions Involving Coreductants

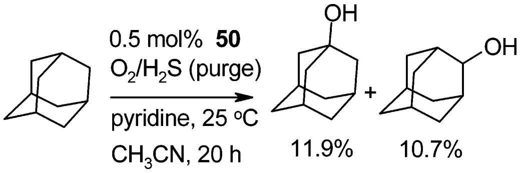
Barton and co-workers extensively studied the oxidation of alkanes since 1983 by Gif systems.[175] These systems exhibit unusual selectivities and occur in pyridine in the presence of an organic acid and iron as the catalyst. For example, the oxidation of cyclohexane has been carried out into a mixture of cyclohexanol and cyclohexanone in 36% conversion using $FeCl_3$ in the presence of hydrogen sulfide and picolinic acid (Scheme 66).[175j] This system functions at ambient temperature in acetonitrile under nearly neutral pH, and the hydrogen sulfide is oxidized to sulfide. Stavropoulos and co-workers studied the oxidation of a series of alkanes to a mixture of alcohols and ketones using iron catalyst in the presence of zinc powder in pyridine and acetic acid mixture (10:1 v/v).[176]

All Gif systems have the same chemical peculiarities: (i) the major products of the reaction are ketones, and alcohols are not reaction intermediates; (ii) the presence of an excess of some easily oxidizable compounds (ROH and RCHO) does not significantly suppress the alkane oxidation; (iii) the selectivity of oxidation for branched hydrocarbons is secondary > tertiary > primary; (iv) secondary alkyl free radicals are not reaction intermediates; (v) alkenes are not epoxidized; and (vi) the addition of trapping reagents can divert the reaction to form monosubstituted alkyl derivatives instead of ketones.

Scheme 66



Scheme 67

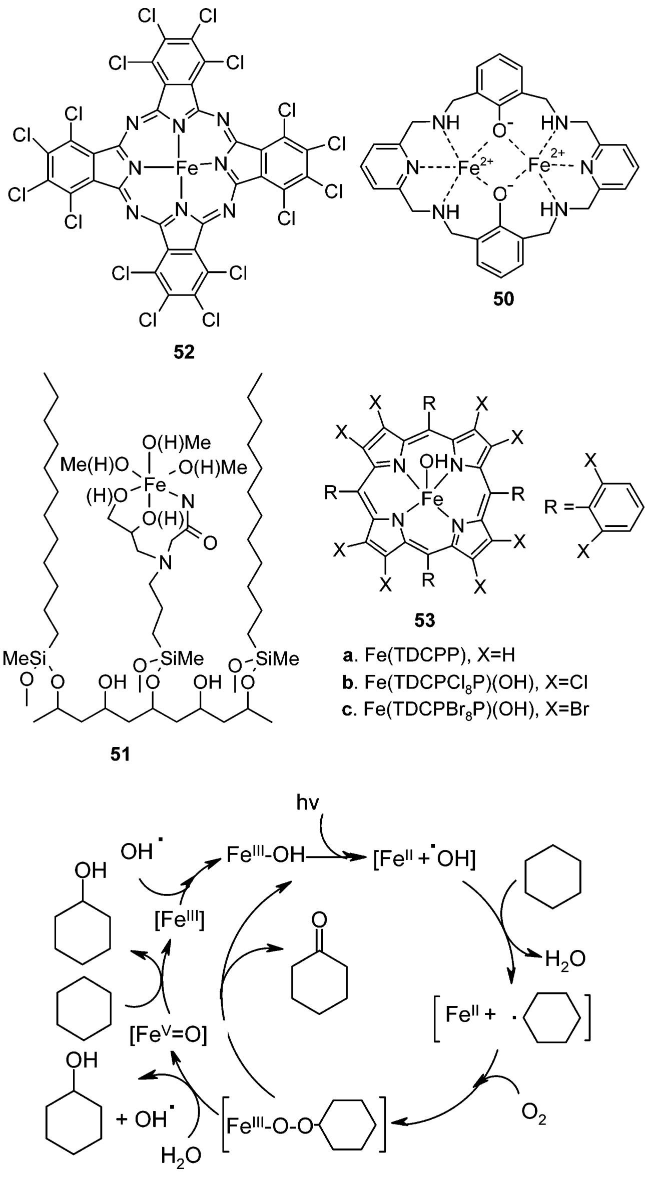


Several studies have subsequently focused on the aerobic oxidation of alkanes using various iron catalysts. Most of these reactions are focused on the oxidation of cyclic alkanes in the presence of PPh_3, sulfides, and aldehydes. The silica-supported iron complex **51** has been shown to catalyze selectively the oxidation of cyclohexane to cyclohexanol with 108 TON in the presence of propane-1,3-dithiol and PPh_3.[177] Martell and co-workers carried out the oxidation of cyclohexane and adamantane using **50** in the presence of hydrogen sulfide and pyridine (Scheme 67).[178] Cyclohexane is oxidized to a 2:1 mixture of cyclohexanol and cyclohexanone with 36 TON, whereas adamantane is converted into a 5:4 mixture of adamantan-3-ol and adamantan-2-ol with 45 TON. Similarly, the iron–porphyrin complex,[179] Fe(TPFPP)Cl, the halogenated phthalocyanine iron(II) complex[180] **52** and iron nanoparticles[181a–c] have been shown to catalyze the oxidation of cyclohexane into a mixture of cyclohexanol and cyclohexanone in the presence of aliphatic aldehydes.

7.3.3. Photooxygenation Reactions

Shul'pin and co-workers extensively studied the oxidation of alkanes using $FeCl_3$ and $Fe(ClO_4)_3$ with atmospheric oxygen under irradiation.[182] Hydroperoxide is proposed as the intermediate for these reactions, which undergoes decomposition to alcohol and aldehyde/ketone. The ratio of alcohol and aldehyde/ketone depends on the reaction conditions. Maldotti and co-workers reported the selective oxidation of cyclohexane using **53** under irradiation in the presence of molecular oxygen (0.2–1 atm) at ambient temperature.[183] The product distribution depends on the reaction conditions. Oxidation of neat cyclohexane using **53a** provides only cyclohexanol, whereas the use of a polar solvent (CH_2Cl_2) with phenyl *tert*-butylnitrone (pbn) leads to exclusive formation of

Scheme 68



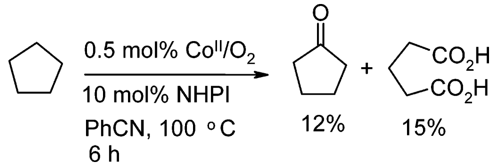
cyclohexanone. This significant difference in their selectivity could be due to the formation of different species (cleavage of O−O bonds) in polar and nonpolar media (Scheme 68). Iron(III)−porphyrins have been shown to catalyze the oxidation of alkane to a mixture of alcohol and ketone (the alcohol/ketone ratio ranges from 0.8 to 2.7) in the presence of triethanolamine.[184]

7.4. Cobalt Catalysts

Cobalt-based catalysts are mainly studied for the partial oxidation of alkanes to alcohols and ketones.

7.4.1. Reactions without Coreductants

Scheme 69



The aerobic oxidation of alkanes catalyzed by Co(OAc)$_3$ has been thoroughly investigated due to its relevance to industrial homolytic oxidation processes.[185] The weakly solvated complex containing acetonitrile, [Co(CH$_3$CN)$_4$](PF$_6$)$_2$, catalyzes the oxidation of adamantane and cyclohexane at 75 °C.[186] The commercial catalyst for cyclohexane oxidation does not function under these conditions. In these reactions, the metal ions function as an initiator as well as a hydroperoxide decomposition catalyst. Ishii and co-workers studied the oxidation of alkanes into a mixture of ketones and carboxylic acids in moderate to high yields by the combined use of Co(acac)$_2$ and NHPI in CH$_3$COOH at 40−100 °C (Scheme 69).[187a,b] Co−AlPO-5 and Co−AlPO-11 with different cobalt contents have been shown to catalyze the autoxidation of neat cyclohexane.[187c] At 130 °C in neat cyclohexane, cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone are formed (8% conversion and 94% selectivity) in a ratio of free radical reaction. The Co−AlPO-18 catalyzes the oxidation of *n*-hexane to adipic acid (9.5% conversion and 32% selectivity) under molecular oxygen.[187d] It is unclear whether the unusual selectivities are solely a consequence of framework effects or due to a direct reaction of the strongly oxidizing Co^{3+} with the hydrocarbon. However, these catalysts can be recycled without loss of activity.

7.4.2. Reactions Involving Coreductants

Few studies are focused on the use of cobalt(II) catalysts for the oxidation of alkanes in the presence of aliphatic aldehydes and molecular oxygen. The complexes **54**[188] and **29a**[189] have been shown to catalyze the oxidation of alkanes into a mixture of alcohols and ketones in the presence of acetaldehyde and 2-methylpropanal, respectively. Similarly, cobalt nanoparticles catalyze the oxidation of neat adamantane and cyclohexane into a mixture of alcohols and ketones in 57−67% conversion in the presence of 2-methylpropanal and molecular oxygen.[181a] These systems are as effective as the iron nanoparticles catalyzed protocols.

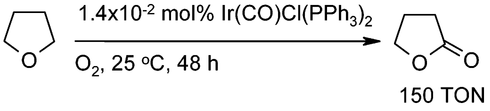
7.5. Iridium Catalyst

The oxidation of neat THF has been studied using IrCl(CO)(PPh$_3$)$_2$ at ambient conditions.[190] γ-Butyrolactone is formed with 150 TON along with a trace lactol and 4-hydroxybutyraldehyde (Scheme 70).

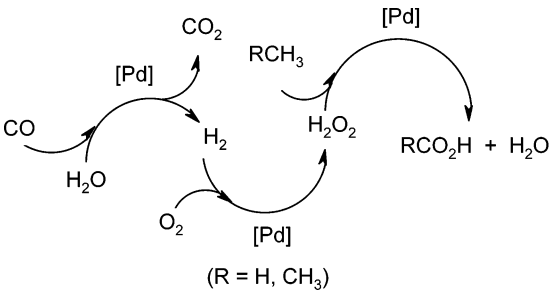
7.6. Palladium Catalysts

A bimetallic catalytic system consisting of metallic palladium and CuCl$_2$ is applied for the low-temperature selective oxidation of methane, ethane, and propane with molecular oxygen (Scheme 71).[191] It operates in a 3:1 mixture (v/v) of trifluoroacetic acid and water in the presence of molecular oxygen and CO. Methane is selectively converted to methanol

Scheme 70



Scheme 71



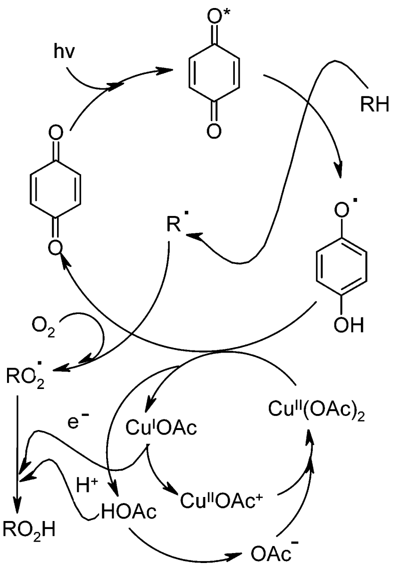
(216 TON based on Pd), whereas both C−H and C−C cleavage products are observed for ethane and propane, resulting in the formation of methanol, ethanol, and acetic acid. The rate of formation of methanol from methane with the bimetallic system is ~65 × 10^{-4} M/min at 145−150 °C. This rate may be compared to the rate of formation of acetic acid from methanol in the benchmark Monsanto process: 380 × 10^{-4} M/min at 180 °C.

The modification of Gif-type reactions using hydrogen peroxide formed in situ by the palladium-catalyzed combining of oxygen and hydrogen is reported.[192a] The oxidation of cyclohexane in the solvent mixture, acetone−acetic acid, gives cyclohexanol and cyclohexanone in rather high yields, but any solvent containing pyridine is not suitable for this modified system. The oxidation of methane to acetic acid is reported in concentrated H_2SO_4 using a combination of $PdSO_4$, $CuCl_2$, and molecular oxygen.[192b] $CuCl_2$ and molecular oxygen appear to promote the rate of oxidation of Pd(0) to Pd(II) during the catalytic cycle, thereby inhibiting the deposition of palladium black.

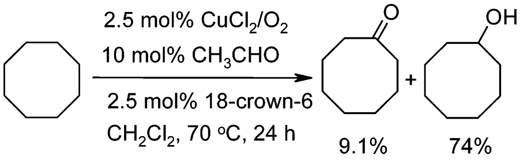
7.7. Copper Catalysts

Most of the copper-catalyzed oxidation of alkanes has been performed in the presence of coreductants. Neckers and Kurusu investigated the oxidation of cyclohexane into a 3.3:1 mixture of cyclohexanol and cyclohexanone in 4.3% conversion (134 TON) by the copper complex immobilized on silica gel in the presence of zinc powder and acetic acid under molecular oxygen.[193] Shul'pin and coworkers reported the oxidation of cyclohexane into a 50:1 mixture of cyclohexanol and cyclohexanone by the combined use of quinone and $Cu(OAc)_2$ (ratio 5:1) in acetonitrile with air and PPh_3 under irradiation (Scheme 72).[194] In this reaction, cyclohexyl hydroperoxide is formed first, which, on reaction with PPh_3, gives cyclohexanol and Ph_3PO. The complex consisting of $CuCl_2$−crown ether catalyzes the oxidation of cyclohexane, cyclooctane, and *n*-hexane to their corresponding alcohols and ketones in 9330−18600 TON in the presence of acetaldehyde under atmospheric oxygen (Scheme 73).[195a] These are high turnovers in the aerobic oxidation of unactivated alkanes, whereas the oxidation of *n*-hexane to a mixture of hexan-1-ol and hexanal in 10.2% conversion catalyzed by the zeolite (NaY) supported copper−perchlorophthalocyanine operates without a coreductant under molecular oxygen.[195b] Remarkably, the oxidation takes place only at the primary CH_3 group. This unusual product distribution weighs strongly against a free radical mechanism, which would normally be expected for a copper-catalyzed oxidation reaction.

Scheme 72



Scheme 73



7.8. Gold Catalysts

Oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone is reported over calcined Au/ZSM-5 molecular sieve with molecular oxygen.[195b] The best result available with this catalyst is 16% conversion (2242 TON) and 92% selectivity at 150 °C. This reaction operates in a solvent-free system, and the catalyst can be recycled twice without loss of activity.

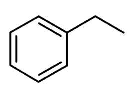
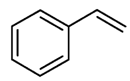
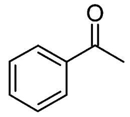
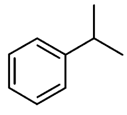
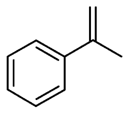
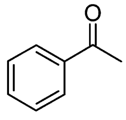
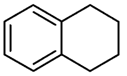
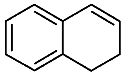
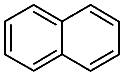
7.9. Platinum Catalyst

Neumann and co-workers reported the oxidation of methane into a mixture of methanol (46%), formaldehyde (9%), and acetaldehyde (41%) in 33 TON using $[Pt(bipyrimidinyl)Cl_2]^+[H_4PV_2Mo_{10}O_{40}]^-/SiO_2$ and molecular oxygen.[195c] The most likely scenario for acetaldehyde formation is the oxidation of methane to formaldehyde via methanol, followed by its coupling with methane to yield the product, possibly occurring entirely in the coordination sphere of the catalyst.

8. Benzylic Oxidation

Benzylic oxidation is an important and fundamental functional transformation in industrial chemistry.[196] Several reagents and methods have been developed for this purpose. This section covers the various catalytic systems that have been used for the oxidation of benzylic substrates with molecular oxygen and transition metal catalysts.

Table 11. Oxidation of Alkylbenzenes Catalyzed by $H_2F_6NaVW_{17}O_{56}^{8-}$ [a]

entry	substrate	TON	products (%)	
1		650	 16	 86
2		3750	 51	 46[b]
3		1250	 45	 55

[a] Substrate (100 mmol) and catalyst (0.02 mmol) were stirred in 10 mL of acetate buffer (pH ~5) under 5 atm of O_2 at 120 °C for 16 h. [b] 3% 2-phenyl-2-propanol formed.

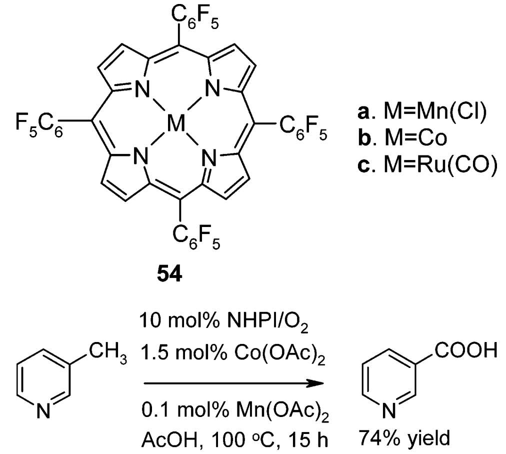
8.1. Vanadium Catalysts

Vanadium-based polyoxometalates have been shown to catalyze efficiently the oxidation of benzylic substrates under oxygen atmosphere.[197] Neumann and co-workers reported the oxidation of alkylbenzene by the Keggin-type polyfluorooxometalate, $[H_2F_6NaV^VW_{17}O_{56}]^{8-}$, in a biphase system (water–catalyst and substrate) (Table 11).[197a] The substrates having secondary and tertiary benzylic C–H bonds are oxidized to a mixture of the corresponding alcohols and ketones in high TON, whereas the substrates with primary C–H bonds mainly give alkenes due to the oxidative dehydrogenation (ODH). The polyoxometalate, V–Cs–Cu–Tl, has been subsequently shown to catalyze the oxidation of toluene to benzaldehyde with 16.5% yield.[197b]

8.2. Manganese Catalysts

Ishii and co-workers studied the oxidation of 3-methylpyridine and methylquinoline by the combined use of $Mn(OAc)_2$, $Co(OAc)_2$, and NHPI in the presence of a small amount of NO_2 as an initiator in CH_3COOH (Scheme 74).[198a,b] This method selectively oxidizes the methyl group to aldehyde in 60–75% yield without affecting the N atom of the substrate. Ratnasamy and co-workers reported the oxidation of *p*-xylene to terephthalic acid in 99.4% yield using a recyclable zeolite-encapsulated Co/Mn cluster with molecular oxygen,[198c] whereas the reaction using the manganese porphyrin complex **54a** catalyzes the oxidation of ethylbenzene to a 3:14 mixture of phenylethanol and acetophenone in the presence of acetaldehyde and molecular oxygen (Scheme 75).[188]

Scheme 74



Scheme 75

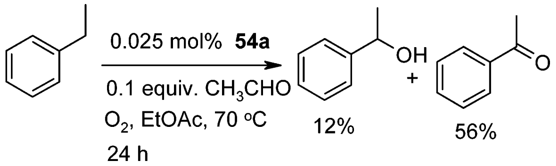


Table 12. Catalytic Activity of Halogenated Iron Complexes in the Oxidation of Ethylbenzene by Oxygen at 100 °C (Reprinted with Permission from Reference 198d. Copyright 2000 Royal Society of Chemistry)

entry	catalyst	catalyst lifetime (h)	catalyst $t_{1/2}$ (h)	TON[a]	TOF (h^{-1})
1	Fe(TPFPP)Cl	1.50	0.5	2900	2000
2	Fe(TTFNMe$_2$PP)Cl	20.00		14000	1000
3	Fe(TTFOPhPP)Cl	0.80	0.2	2000	3000
4	Fe(TPFPP-Br$_8$)Cl	0.75	0.2	4700	6500
5	Fe(TPFPP-Cl$_8$)Cl	0.75		5000	9200
6	Fe(TDCPP-Cl$_8$)Cl	1.50	0.3	5000	6500
7	[Fe(TPFPP)]$_2$O		60.0	25000[b]	1300

[a] Before complete destruction of the catalyst. [b] Turnovers at $t_{1/2}$.

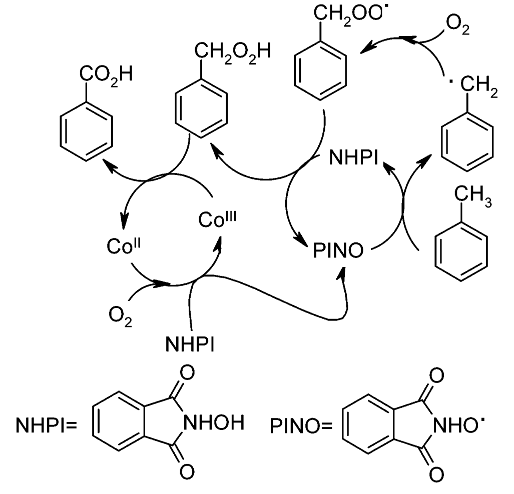
8.3. Iron Catalysts

Evans and Smith studied the oxidation of ethylbenzene using iron–haloporphyrins in a solvent-free system under molecular oxygen at 30–110 °C (Table 12).[198d] A mixture of hydroperoxide, phenylethanol, and acetophenone is obtained with up to 25000 TON using the μ-oxocomplex $[Fe(TPFPP)]_2O$ [TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin]. They have subsequently supported $FeTF_4PP$ [TF_4PP = tetrakis(pentafluorophenyl)porphyrin] on SiO_2 and polystyrene to afford $SiFeTF_4PP$ and PS–$FeTF_4PP$ **55**, which catalyze the oxidation of ethylbenzene to a mixture of alcohol, ketone, and hydroperoxide in 7400 TON.[198e] Murahashi and co-workers reported the oxidation of ethylbenzene using Fe powder, $Fe(OAc)_3$, and $FeCl_3$ in the presence of *n*-heptanal and acetic acid.[198f] Fe powder is found to be more effective, affording a mixture of phenylethanol and acetophenone in good conversion. A high-valent iron–oxo species is proposed as a key intermediate for this system.

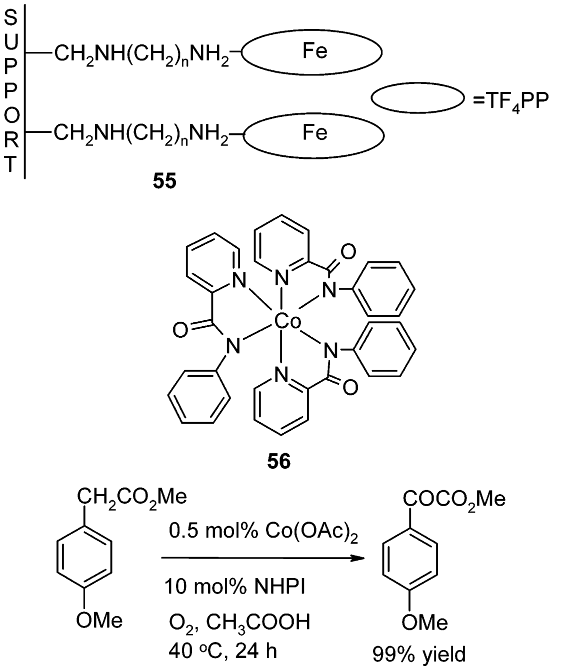
8.4. Cobalt Catalysts

Cobalt catalysts have been extensively studied for the C–H oxidation of alkylbenzenes with molecular oxygen. The oxidation of alkylbenzenes with cobalt/bromine,[199a] $CoCl_2$/diglyme,[199b] and cobalt with dipyridyl- and acetylacetone-functionalized polymers[199c] with molecular oxygen has been recently reviewed.[1c]

Scheme 76



Scheme 77



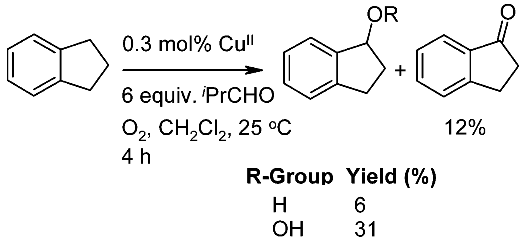
Cobalt complex **56** has been shown to catalyze the oxidation of neat ethylbenzene to acetophenone in 70% conversion and 90% selectivity.[200a] Ishii and co-workers described the oxidation of alkylbenzenes by the combined use of Co(acac)$_{n=2,3}$ and NHPI in acetic acid.[200b-d] The substrates having primary benzylic C−H bonds are oxidized to carboxylic acids, and secondary and tertiary C−H bonds are converted to a mixture of ketones and alcohols in quantitative yield (Scheme 76). Acetic and mandelic acid esters are oxidized to the corresponding α-ketoesters in quantitative yields (Scheme 77).[201a] Tsang and co-workers reported the oxidation of toluene to benzoic acid (>99% conversion and >99% selectivity) using the fluorous tag Co(II)/NaBr in a water and supercritical CO_2 mixture,[201b] whereas Co/Mn/Br$^-$ (1:3:10) catalyzes the oxidation of *p*-cymene, *p*-methoxytoluene, and *p*-*tert*-butyltoluene in water−dioxane under air to provide a mixture of products in moderate conversion.[201c]

Table 13. Aerobic Oxidation of Alkylbenzenes Using $CuCl_2$−Crown Ether[a]

		yield (%)		
entry	alkylbenzene	alcohol	ketone	TON
1	ethylbenzene	2	13	3480
2	indane	11	50	14100
3	tetraline	9.2	56	14800

[a] A mixture of $CuCl_2$ (1×10^{-4} mmol) and 18-crown-6 (1×10^{-4} mmol) in CH_2Cl_2 was added to alkylbenzene (40 mmol), acetaldehyde (4 mmol), and the resultant solution stirred in an autoclave under O_2 (1 atm) for 24 h.

Scheme 78



8.5. Copper Catalysts

The copper-catalyzed benzylic oxidations operate in the presence as well absence of coreductants.

8.5.1. Reactions without Coreductants

Copper(II) chloride, in combination with acetoxime, has been shown to catalyze the oxidation of a methyl group in 2,4,6-trimethylphenol in alcohols at ambient temperature.[202] Xu and co-workers reported the oxidation of *p*-cresol to *p*-hydroxybenzaldehyde with up to 95.6% selectivity at 98.5% conversion.[203a] This reaction has been performed in an autoclave in the presence of sodium hydroxide in methanol under molecular oxygen.

8.5.2. Reactions Involving Coreductants

The oxidation of ethylbenzene, indane, and tetraline has been performed with $CuCl_2$−crown ether in the presence of acetaldehyde and molecular oxygen.[195a] These systems are efficient, and the corresponding alcohols and ketones are obtained in high TON (Table 13). The crown ether is believed to stabilize the oxometal intermediate by coordination and prevents its self-decomposition before hydrogen abstraction of hydrocarbons. A metal−oxo intermediate has been proposed as the key intermediate in these oxidations. The oxidation of indane to indanol (6%), indan-1-yl hydroperoxide (31%), and indanone (12%) is reported using copper salts, $Cu(OH)_2$, $CuCl_2$, and $Cu(TPIP)_2$, in the presence of 2-methylpropanal and molecular oxygen (Scheme 78).[203b] There is no reaction in the presence of TEMPO, indicating that this system occurs via a radical pathway and not by a metal−oxo intermediate.

9. Aromatic C−H Oxidation

The aromatic C−H oxidation remains one of the most challenging problems in organic synthesis. The aromatic nucleus is resistant to oxidation because of its resonance stabilization, so oxygenation almost

Table 14. Oxidation of Benzene to Phenol Using Various Transition Metal Catalysts under Molecular Oxygen

entry	catalyst	coreductant	ref
1	VO(dmp)$_2$	crotonaldehyde	205
2	(n-Bu)$_4$NVO$_4$	zinc powder	206a
3	V/TiO$_2$	zinc powder	206b
4	ReO$_4$/H-ZSM-5	none	207
5	**58**	zinc powder	208a
6	FeCl$_2$-H$_3$PW$_{12}$O$_{40}$	L-ascorbic acid	208b
7	Pd(OAc)$_2$-phenanthroline	CO	211a
8	Pd-Nafion/SiO$_2$	H$_2$	211c
9	Pd-membrane	H$_2$	211e
10	Pt/V$_2$O$_5$	H$_2$	213
11	CuCl$_2$/Pd(OAc)$_2$	H$_2$	214
12	Cu-MCM	L-ascorbic acid	215a

invariably requires a highly reactive oxidant under severe conditions.[204] During recent years several studies have appeared using transition metal catalysts with molecular oxygen for the aromatic C−H oxidation. This section covers the aerobic oxygenation as well as the oxidative coupling of aromatic systems. The studies on the oxidation of benzene to phenol are summarized in Table 14.

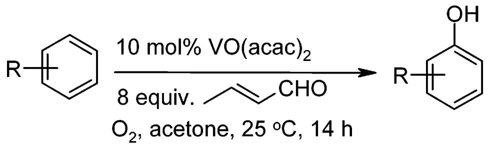
9.1. Vanadium Catalysts

Vanadium-based catalysts have been studied for the hydroxylation as well as oxidative coupling of aromatic compounds.

9.1.1. Hydroxylation of Benzene Derivatives

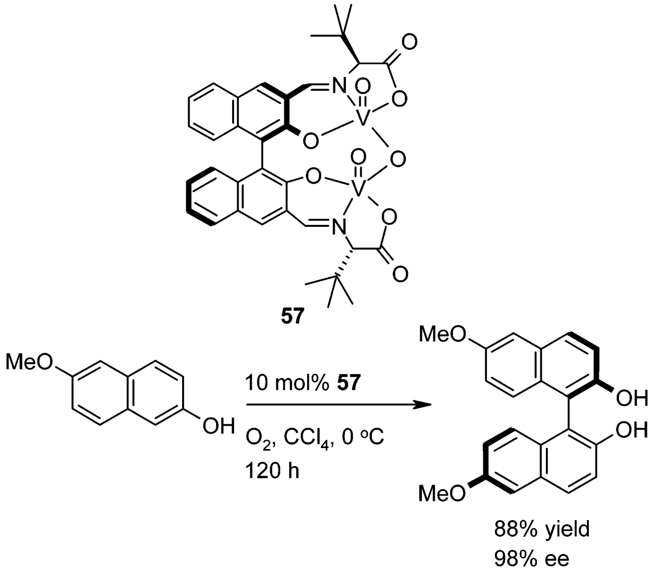
Following the vanadium-catalyzed aerobic epoxidation of alkenes,[10a] Mukaiyama and co-workers reported the hydroxylation of substituted benzenes using VO(dpm)$_2$ [dmp = 1,3-bis(p-methoxyphenyl)-1,3-propanedionato] in the presence of crotonaldehyde and atmospheric oxygen (Scheme 79).[205] Under these conditions, naphthalene is oxidized into 1,4-naphthaquinone without forming any phenolic compound. Shul'pin and co-workers carried out the oxidation of benzene to phenol using (n-Bu)$_4$NVO$_3$ in acetonitrile in the presence of solid ascorbic acid and with obligatory participation of pyridine, pyrazine-2-carboxylic acid, and acetic acid as mediators of proton and electron transfer.[206a] If some water is added to the system, the compound dissolves in aqueous acetonitrile and no hydroxylation occurs. The oxidation of naphthalene under the same reaction conditions gives isomeric naphthols (α/β = 4:1). Ascorbic acid can be replaced with zinc powder, and the zinc-based system hydroxylates not only benzene and aromatic ring methyl group in toluene ($o/m/p$ = 47:28:25) but also C−H bonds in cyclohexane with the total TON being 78. The supported vanadium catalysts, V/SiO$_2$ and V/TiO$_2$, have been shown to catalyze the oxidation of benzene to phenol in 3.7% yield in the presence of zinc and molecular oxygen.[206b] In these reactions, some of the vanadium leaches into solution; this amount can be decreased by cosupporting Cu on the catalyst.

Scheme 79



R-Group	Yield (%) (*ortho/meta/para*)
H	21
^{t}Bu	31 (23/35/43)
Ph	18 (33/17/50)
Cl	17 (32/0/68)

Scheme 80



9.1.2. Oxidative Coupling of 2-Naphthols

Optically active binaphthol (BINOL) and its derivatives are used as chiral auxiliaries and ligands in asymmetric synthesis and show an extremely high stereocontrol property in a wide range of asymmetric transformations.[206c] Few studies are focused on the synthesis of these compounds by enantioselective oxidative coupling using chiral oxovanadium(IV) complexes and molecular oxygen.[206d,e] The substrates containing an electron-donating group or unsubstituted 2-naphthol provide high enantioselectivity (Scheme 80).

9.2. Rhenium Catalysts

Zeolite (H−ZSM-5) supported ReO$_4$ has been investigated for the oxidation of benzene to phenol in the presence of molecular oxygen at 300 °C.[207] In this reaction the presence of NH$_3$ is indispensable for reducing and stabilizing the Re species efficiently.

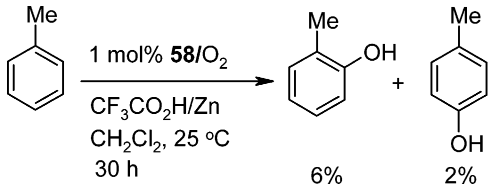
9.3. Iron Catalysts

Iron catalysts have been studied for the aerobic hydroxylation of benzene derivatives at ambient temperature. The bimetallic iron complex **58** is catalyzed the oxidation of benzene to phenol in 11% yield in the presence of zinc powder.[208a] By this method toluene can be oxidized to a 2:5 mixture of o- and p-methylphenol in 8% yield (Scheme 81). The catalytic system consisting of FeCl$_2$ and H$_3$PW$_{12}$O$_{40}$ is catalyzed the hydroxylation of benzene in 27% yield in the presence of ;-ascorbic acid.[208b]

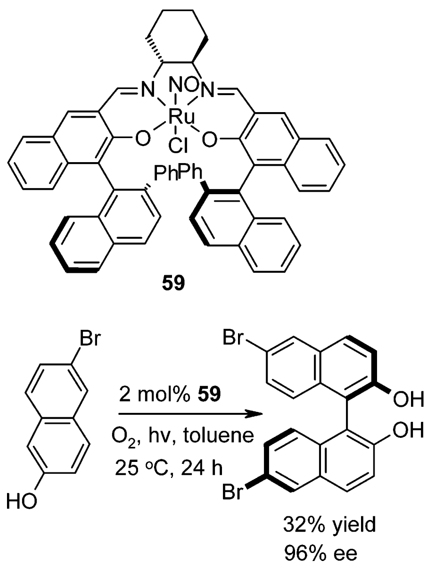
9.4. Ruthenium Catalysts

Ruthenium complexes catalyze the oxidative coupling of aromatic compounds with molecular oxygen.

Scheme 81



Scheme 82



The oxidation of 2-naphthols to optically active BINOLs using chiral Ru–salen complex **59** is reported (Scheme 82).[209a] This reaction functions in the presence of light, and the substrate with a Br substituent has shown the highest enantioselectivity (up to 96% ee). Milstein and co-workers carried out the oxidative coupling of aryl systems with alkenes in the presence of ruthenium salts and molecular oxygen.[209b] These reactions are effective in the presence of CO at high temperature (180 °C) under 2 atm of molecular oxygen. By this method, (*E*)-methyl cinnamate can be obtained in 41% yield (88 TON) from benzene and methyl acrylate.

9.5. Cobalt Catalysts

The oxidative coupling of phenol to diphenoquinones is reported with layered double hydroxide (LDH) supported Co–phthalocyanines and molecular oxygen.[210] The intercalation in the LDH stabilizes the catalyst against self-destruction. Whereas only 25 TON can be achieved in solution, the LDH-supported species remains stable after >3200 TON.

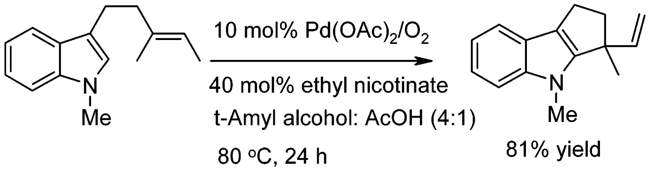
9.6. Palladium Catalysts

Palladium complexes catalyze efficiently the hydroxylation as well as oxidative coupling of aromatic compounds.

9.6.1. Hydroxylation of Benzene

The palladium-catalyzed hydroxylation reactions are focused on the oxidation of benzene to phenol. Pd(OAc)$_2$–phenanthroline is used for the oxidation of benzene to phenol in the presence of molecular oxygen and CO.[211a,b] The solid-supported palladium catalysts Pd/Ts-1[211c] and Pd–Nafion/SiO$_2$ composite[211d] and palladium membrane[211e] catalyze the oxidation of benzene to phenol under oxygen and hydrogen atmosphere. The reaction using palladium membrane shows the best result, 13.3% conversion and 85.5% selectivity. It uses a shell-and-tube reactor, in which a gaseous mixture of benzene and oxygen is fed into a porous alumina tube coated with a palladium thin layer and hydrogen is fed into the shell. Hydrogen dissociated on the palladium layer surface permeates onto the back and reacts with oxygen to give active oxygen species, which attack benzene to produce phenol.

Scheme 83



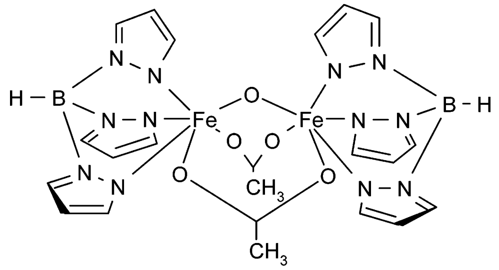
9.6.2. Oxidative Coupling Reactions

The oxidative coupling of benzene to biphenyl catalyzed by Pd(OAc)$_2$ is reported in 3.4% conversion and 88% selectivity in the presence of a molybdenum cocatalyst.[212a] Ishii and co-workers described the oxidative coupling of benzene with alkenes bearing an electron-withdrawing groups using Pd(OAc)$_2$ and polyoxometalate, HPMoV.[212b] This catalytic system can be extended to the coupling reactions between various substituted benzenes and alkenes. Jacobs and co-workers showed a high catalytic activity (up to 762 TON) in the reaction between benzene derivatives and electron-deficient alkenes using Pd(OAc)$_2$ in the presence of PhCOOH.[212c] Ferreira and Stoltz described the intramolecular cyclization of homoallyl indole using Pd(OAc)$_2$ in the presence of substituted pyridine (Scheme 83).[212d] The nature of the pyridine derivative and palladium source has a considerable effect on the catalysis.

9.7. Platinum Catalysts

Platinum catalysts have been investigated for the hydroxylation of benzene under oxygen and hydrogen atmosphere. Benzene is oxidized to phenol selectively without forming any carbon oxides on supported platinum catalyst with V$_2$O$_5$ or Pd cocatalyst.[213] The reaction proceeds both in liquid phase in the presence of acetic acid at 20–60 °C and in gas phase at elevated temperature. Although sufficient yield for industrial production of phenol is obtained, still the consumption of hydrogen gas is not satisfactory in these reactions. The efficiency of oxygen to form phenol is 30–40%, implying that 7–8 mol of hydrogen is consumed to form 1 mol of phenol. Nevertheless, the reductive activation of oxygen is expected to develop new industrial oxidation process for future technology.

Scheme 84

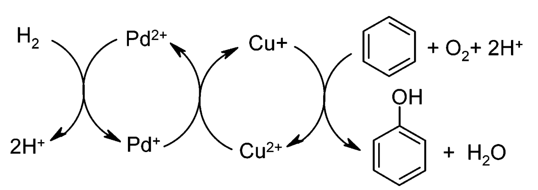


58

$$2Cu^{I} + O_2 + 2H^{+} \longrightarrow 2Cu^{II} + H_2O_2$$

$$Cu^{I} + H_2O_2 + H^{+} \longrightarrow Cu^{II} + HO^{\bullet} + H_2O$$

Scheme 85



9.8. Copper Catalysts

Copper complexes have been studied for the hydroxylation of benzene, the oxidation of phenol to 1,4-quinone, and the oxidative coupling of benzene derivatives.

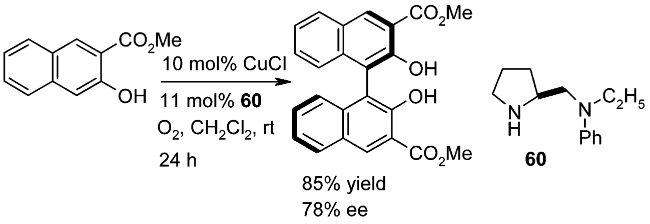
9.8.1. Oxidation of Benzene Derivatives

Copper(I) chloride promotes the oxidation of benzene to phenol with molecular oxygen.[214] The active species is proposed to be a hydroxy radical generated as shown in Scheme 84, but the reaction proceeds catalytically when Cu(II) is reduced to Cu(I) by molecular hydrogen in the presence of a palladium cocatalyst (Scheme 85). Tsuruya and co-workers reported the liquid phase oxidation of benzene to phenol, with molecular oxygen and Cu−zeolite or Cu−MCM as the catalyst.[215a−c] However, phenol yields are low, a large amount of supported Cu is required, and ascorbic acid is used as a stoichiometric coreductant. Phenol production is accompanied by the formation of H_2O_2 in solution. Sun and co-workers carried out the oxidation of 2,3,6-trimethylphenol to trimethyl-1,4-benzoquinone (86% yield).[215d] This reaction is reported in ionic liquid, 1-butyl-3-methylimidazolium chloride, using copper(II) chloride and molecular oxygen.

9.8.2. Oxidative Coupling Reactions

Few studies have focused on the oxidative coupling of 2,6-di-*tert*-butylphenol to 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone using Cu−Mg−Al hydrotalcite[216a] and Cu-exchanged MCM-41[216b,c] catalysts under molecular oxygen. In the presence of chiral amines **47** and **60**, CuCl is catalyzed the oxidative coupling of 2-naphthol to give optically active BINOL in good enantioselectivity (Scheme 86).[216d,e] The substrate with an ester moiety at the 3-position has shown the highest enantioselectivity (<78% ee).

Scheme 86



10. Baeyer−Villiger Oxidation

Baeyer−Villiger oxidation is a frequently used synthetic tool for the conversion of cycloalkanones to lactones. Usually, this transformation is carried out by peroxy compounds such as peracids[217] and ROOH.[218] Acids, bases, enzymes, and metal-containing reagents are known to catalyze Baeyer−Villiger oxidation.[219] This section covers the recent studies of the aerobic Baeyer−Villiger oxidation catalyzed by transition metal salts.

10.1. Manganese and Cobalt Catalysts

Manganese and cobalt aluminophosphates, MAlPO (M = Mn and Co), have been investigated for the Baeyer−Villiger oxidation of ketones in the presence of benzaldehyde and molecular oxygen.[220] The oxidation of cyclopentanone, cyclohexanone, 2-methylcyclohexanone, and adamantan-2-one is performed in high yields (Table 15). After calcination at 550 °C, the recovered catalysts can be recycled without significant loss in catalytic activity.

10.2. Iron Catalysts

Murahashi and co-workers accomplished the oxidation of ketones to lactones with Fe_2O_3 in the presence of benzaldehyde and molecular oxygen in 56−98% yields.[221] This reaction provides a convenient method for the synthesis of 4-acyloxy β-lactams, which are key intermediates for the synthesis of thienamycin and 1-methylcarbapenems. For example, 4-benzoyl lactam **61** has been oxidized to 4-benzoyloxy β-lactam **62** with complete retention of configuration in 93% yield (Scheme 87). These oxidations can be rationalized by assuming two pathways as shown in Scheme 88. The reaction of the aldehyde **a** with molecular oxygen and catalyst would give acylperoxy radical **b**, which is a key intermediate of autoxidation of aldehyde. The radical abstracts hydrogen from aldehyde to give peracid **c**, which undergoes facile reaction with ketone to give **d**. Alternatively, the radical reacts with ketone and subsequently with an aldehyde to give **e**. The intermediate thus formed would undergo rearrangement to give ester **f** and carboxylic acid.

10.3. Nickel Catalysts

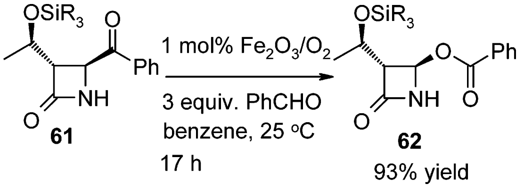
Soon after the discovery of the aerobic epoxidation of alkenes by the combined use of metal complex, aliphatic aldehyde, and molecular oxygen, Mukaiyama and co-workers reported the aerobic Baeyer−Villiger oxidation of cyclic and linear ketones.[222] These reactions have been performed with $Ni(dpm)_2$

Table 15. Baeyer–Villiger Oxidation of Cyclic Ketones with MALPO (M = Mn or Co) (Reprinted with Permission from Reference 220. Copyright 1999 Royal Society of Chemistry)[a]

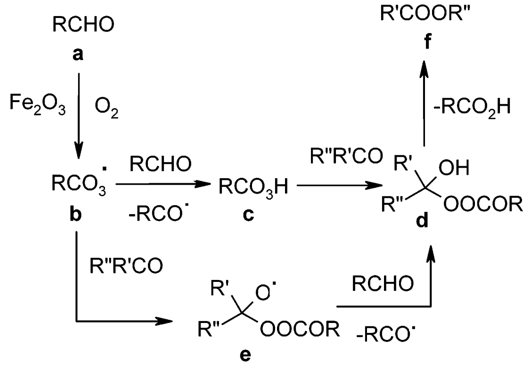
entry	substrate	catalyst	pore dimension (Å)	TOF (h^{-1})	conversion (%)	selectivity (%)
1	cyclopentanone	CoALPO-36	6.5 × 7.5	238	58	92
		MnALPO-36	6.5 × 7.5	246	61	94
2	cyclohexanone	CoALPO-36	6.5 × 7.5	250	71	98
		CoALPO-5	7.3 × 7.3	204	60	80
		MnALPO-36	6.5 × 7.5	257	78	98
		MnALPO-5	7.3 × 7.3	207	64	82
		CoALPO-18	3.8 × 3.8		22	62
		no catalyst			20	65
3	cyclooctanone	CoALPO-36	6.5 × 7.5	238	58	92
		MnALPO-36	6.5 × 7.5	246	61	94
4	adamantan-2-one	CoALPO-36	6.5 × 7.5	201	65	86
		MnALPO-36	6.5 × 7.5	208	72	89

[a] Substrate (~20 g), catalyst (~150 mg), and PhCHO (3 equiv with respect to the substrate) were stirred under O_2 (30 atm) at 50 °C for 6 h.

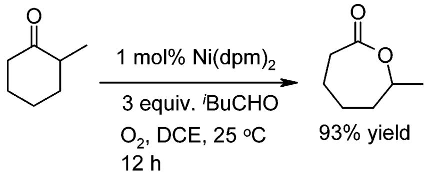
Scheme 87



Scheme 88



Scheme 89

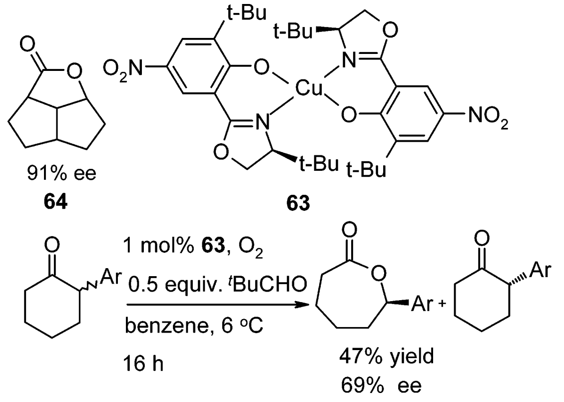


in the presence of isovaleraldehyde at ambient conditions (Scheme 89).

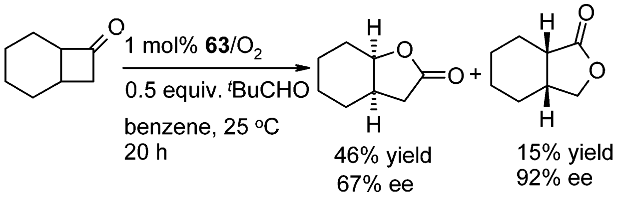
10.4. Copper Catalysts

Bolm and co-workers reported the enantioselective Baeyer–Villiger oxidation of cyclic ketones using copper complex **63** in the presence of pivalaldehyde and molecular oxygen.[223] In the presence of 1 mol % of **63**, racemic 2-phenylcyclohexanone is oxidized to optically active lactone in 41% yield with up to 69% ee, and the unreacted ketone shows *S* configuration (Scheme 90). The best result is observed in benzene solutions at ambient temperature. Chiral cyclobutanone derivatives are oxidized with up to 95% ee (Scheme 91).[223] With respect to cyclohexanones, the scope of this reaction remains limited, and only 2-aryl-substituted compounds are reactive enough to give the corresponding optically active lactones. Prochiral cyclobutanones also give optically active lactones; the enantioselectivity in this process, however, is only moderate (up to 44% ee). The only exception observed is the oxidation of Kelly et al.'s tricyclic ketone, which has afforded lactone **64** in 91% ee.[223b,f]

Scheme 90



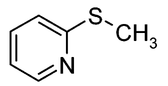
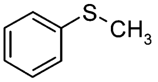
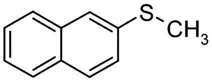
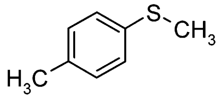
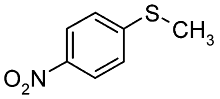
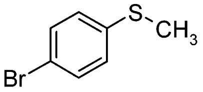
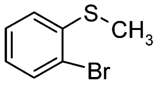
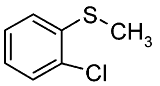
Scheme 91



11. Sulfoxidation

The oxidation of sulfides to sulfoxides has been extensively studied due to the importance of sulfoxides as useful intermediates in organic synthesis, and some of them play key roles in the activation of enzymes.[224] Many oxidants are available to perform this key transformation.[225] This section covers the transition metal catalyzed aerobic oxidation of sulfides.

Table 16. Asymmetric Sulfoxidation Using 13 (Reprinted with Permission from Reference 226. Copyright 1995 Chemical Society of Japan)[a]

entry	sulfide	yield (%)	ee (%)
1		55	24
2		66	51
3		57	51
4		58	44
5		44	69
6		55	61
7		93	70
8		72	72

[a] Sulfide (0.125 mmol), pivalaldehyde (0.375 mmol), and **13** (0.0225 mmol) were stirred in *m*-xylene (5 mL) at 25 °C with 1 atm of O_2 for 20 h.

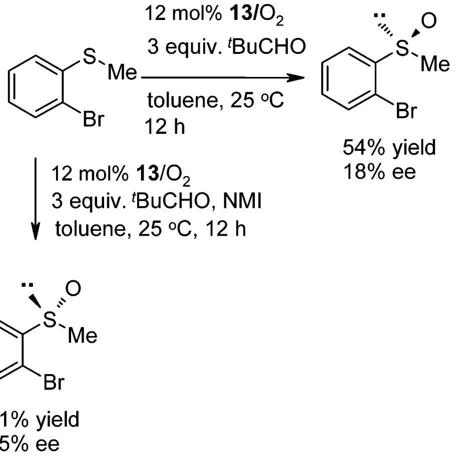
11.1. Vanadium and Molybdenum Catalysts

Haimov and Neumann studied the oxidation of sulfides using a polyoxometalate, $H_5PV_2Mo_{10}O_{40}$, and molecular oxygen in poly(ethylene glycol) at 115 °C.[76e] Tetrahydrothiophene, diphenyl sulfide, dibutyl sulfide, and thioanisole are oxidized to a mixture of the corresponding sulfoxides and sulfones in 33–82% conversion.

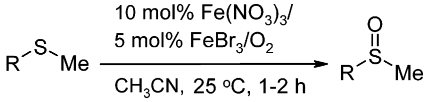
11.2. Manganese Catalysts

Enantioselective sulfoxidation of aryl alkyl sulfides (44–95% ee) has been studied using chiral manganese complexes **9** and **13** in the presence of aliphatic aldehydes and molecular oxygen.[226] The complexes **13** are more effective and catalyze the oxidation of a series of alkyl aryl sulfides with good enantioselectivity (Table 16). The reactivity profile of this sulfoxidation is similar to that of the enantioselective epoxidation of alkenes. For example, the ee of methyl *o*-bromophenyl sulfoxide is dependent on the nature of the aldehyde: *t*-BuCHO, 52% ee; *i*-PrCHO, 46% ee; and *n*-PrCHO, 42% ee. The addition of *N*-alkylimidazole (NAI) is essential in these reactions as its absence leads to low chemical and optical yield of sulfoxide having the opposite enantioselectivity (Scheme 92).

Scheme 92



Scheme 93



R-Group	Time (h)	Yield (%)
^{t}Bu	1.5	82
Ph	1.0	92
4-OMePh	1.5	90
4-BrPh	1.3	90
4-CNPh	1.5	92
4-NO$_2$Ph	2.0	91

11.3. Iron Catalysts

The iron catalysts have been shown to catalyze efficiently the sulfoxidation reaction with molecular oxygen. The oxidation of a series of sulfides has been studied using $Fe(NO_3)_3-FeBr_3$, $Fe(NO_3)_3-FeBr_2$, and $Cu(NO_3)_2-CuBr_2$ under oxygen atmosphere.[227] The binary system, $Fe(NO_3)_3-FeBr_3$, is more active, catalyzing the oxidation of sulfides in high yields. Two types of active species may be considered in this process, either oxidation by NO_2 or oxidation by the bromides/bromine couple controlled by Fe(III) (Scheme 93). Hill and co-workers reported that the silica nanoparticle supported polyoxometalate, $\{K_8[Fe^{III}(OH_2)_2)_3(PW_9O_{34})_2]\}_{58}(Si/AlO_2)$, catalyzes the oxidation of tetrahydrothiophene to tetrahydrothiophene oxide in high TON.[228a] This reaction takes place by autoxidation, and no sulfone is observed. Iron(III)–porphyrin complexes have been studied for the oxidation of dimethyl sulfide to give a mixture of the corresponding sulfoxide (610 TON) and sulfone (68 TON) under irradiation.[228b] Carson and Lippard described the oxidation of pyridylphenyl sulfide tethered to a carboxylate–diiron complex in the presence of molecular oxygen.[228c]

11.4. Nickel Catalysts

Knochel and co-workers reported the oxidation of sulfides using a polyfluoroinated nickel complex in a fluorous biphase system (FBS).[34c] By this method, sulfides can be selectively converted to either sulfoxide or sulfone on the basis of the quantity of the coreductant, 2-methylpropanal. The fluorous phase having the catalyst can be recycled without of loss of activity.

12. Conclusions

The foregoing sections have clearly demonstrated the impressive progress made in the area of transition metal catalyzed aerobic epoxidation of alkenes. The methodologies described based on various epoxidation reactions have clearly opened new avenues for major growth in the area of epoxidation using molecular oxygen. The use of molecular oxygen as a source of oxygen atom and the formation of few neutral byproducts clearly make aerobic oxidation a highly desirable, economically viable, and environmentally acceptable reaction. The epoxidation reaction can be made more attractive if both of the oxygen atoms of the dioxygen can be transferred during the epoxide formation. These epoxidations can further be made environmentally viable by using catalyst anchored on polymer and carrying out the reaction in FBS. This review has also highlighted the remarkable progress made in Wacker oxidation. Clearly the oxidation of the carbon−carbon double bond to the corresponding carbonyl compounds is a highly desirable and rewarding industrial process. Similarly, the progress made in the area of C−H oxidation of alkanes is very impressive, and this will allow access to a rich feedstock for fine chemical industries. The Wacker oxidation and C−H oxidation of alkanes have been successfully performed with environmentally friendly catalysts that can be recycled. This aspect is going to be important for chemical industries from the point of view of environmental consideration. Although transition metal catalyzed allylic and benzylic oxidation have met with little success, the initial studies on this important chemical transformation are encouraging, and it holds a promising future for its application in the fine chemical industry. The limited success achieved during the transition metal catalyzed oxidation of benzene has paved the way for future exploration into this important chemical transformation. This transformation would have a profound impact on the polymer, pharmaceutical, and agrochemical industries. The transitional metal catalyzed aerobic oxidation of sulfides has been successfully achieved by manganese catalysts. This reaction promises to open new avenues for enantioselective synthesis of sulfoxides.

Finally, transition metal catalyzed oxidation of organic substrates with molecular oxygen is becoming an important and highly rewarding protocol for important feedstocks for fine chemical industries. Initial success in this area is promising and forecasts future growth in accessing oxidized organic molecules using molecular oxygen and transition metal catalysts. The efforts in this area will clearly culminate in tackling the major issues pertaining to environmentally acceptable technologies for future.

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