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New developments in catalytic alcohol oxidations for fine chemicals synthesis

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Abstract

New developments in liquid phase catalytic oxidations of alcohols with O_2 and H_2O_2 as the primary oxidant are reviewed. Both homogeneous and heterogeneous catalysts are discussed and compared and emphasis is placed on methods having broad utility for the synthesis of fine chemicals. Mechanistic features of the various systems are also discussed, e.g., oxometal vs. peroxometal pathways in oxidations with H_2O_2 and oxometal vs. hydridometal pathways with O_2 as the oxidant. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic oxidations; Oxometal and peroxometal pathways; Hydrogen peroxide; Molecular oxygen; Hydrometal pathway

1. Introduction

The oxidation of primary and secondary alcohols into the corresponding carbonyl compounds plays a central role in organic synthesis [1–3]. Traditional methods for performing such transformations generally involve the use of stoichiometric quantities of inorganic oxidants, notably chromium(VI) reagents [4]. However, from both an economic and environmental viewpoint there is a growing demand for atom efficient, catalytic methods that employ clean oxidants such as O_2 and H_2O_2. For use in fine chemicals synthesis it is also important that such methods are broad in scope, i.e., are effective with a broad range of alcohols that often contain other functional groups, e.g., olefinic double bonds and heteroatoms, that are sensitive to oxidation.

2. Mechanisms

Metal-catalyzed oxidations with hydrogen peroxide can be conveniently divided into two categories, involving peroxometal and oxometal species, respectively, as the active oxidant [5]. This is illustrated for alcohol oxidations in Fig. 1 [6]. In the peroxometal pathway the metal ion does not undergo any change in oxidation state during the catalytic cycle and no stoichiometric oxidation is observed in the absence of H_2O_2. In contrast, oxometal pathways involve a two electron change in oxidation state of the metal ion and a stoichiometric oxidation is observed, with the oxidized state of the catalyst, in the absence of H_2O_2. Indeed, this is a test for distinguishing between the two pathways.

Peroxometal pathways are typically observed with early transition metal ions with a d^0 configuration, e.g., Mo(VI), W(VI), Ti(IV), Re(VII), that are relatively weak oxidants. Oxometal pathways are characteristic of late transition elements and first row transition elements, e.g., Cr(VI), Mn(V), Os(VIII),

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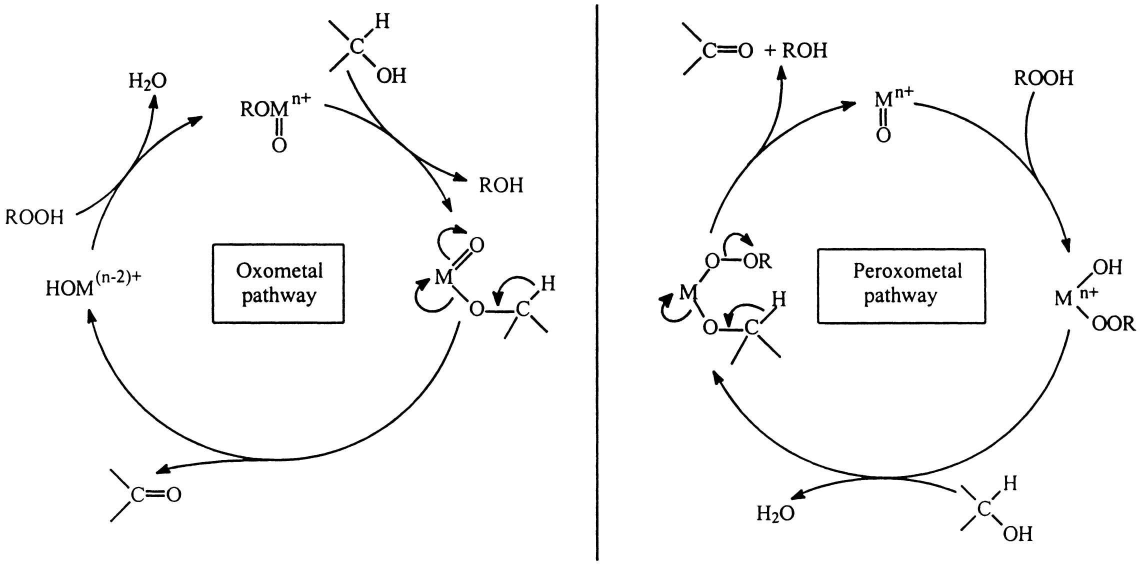


Fig. 1. Alcohol oxidation; oxometal vs. peroxometal pathways.

Ru(VI) and Ru(VIII), that are strong oxidants in their highest oxidation states. Some metals can operate via both pathways depending, *inter alia*, on the substrate, e.g., vanadium(V) operates via a peroxometal pathway in olefin epoxidations and via an oxometal pathway in alcohol oxidations [1].

In aerobic oxidations of alcohols a third pathway is possible with late transition metal ions, particularly those of Group VIII elements. The key step involves dehydrogenation of the alcohol, via β-hydride elimination from the metal alkoxide to form a metal hydride (see Fig. 2). This constitutes a commonly employed method for the synthesis of such metal hydrides. The reaction is often base-catalyzed which explains the use of bases as cocatalysts in these systems. In the catalytic cycle the hydridometal species is reoxidized by O_2, possibly via insertion into the M–H bond and formation of H_2O_2. Alternatively, an alkoxymetal species can afford a proton and the reduced form of the catalyst, either directly or via the intermediacy of a hydridometal species (see Fig. 2). Examples of metal ions that operate via this pathway are Pd(II), Ru(II) and Rh(III).

We note the close similarity of the β-hydride elimination step in this pathway to the analogous step in the oxometal pathway (see Fig. 1). Some metals, e.g.,

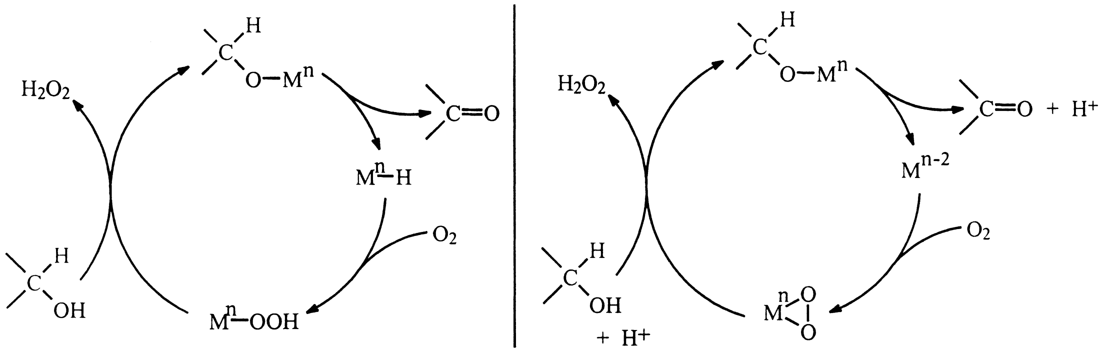


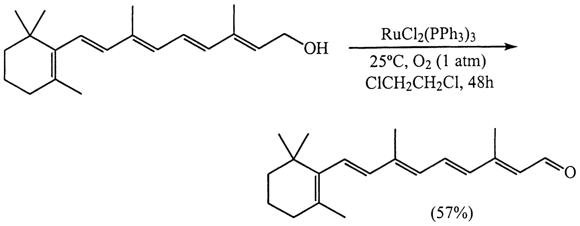
Fig. 2. Hydridometal pathways for alcohol oxidation.

ruthenium, can operate via both pathways and it is often difficult to distinguish between the two.

A further variation on the hydridometal pathway is observed with supported noble metal catalysts, e.g., palladium or platinum on activated charcoal. In this case the zerovalent metal dehydrogenates the alcohol to form surface metal hydrides that subsequently react with O_2 to regenerate the metal. Indeed, platinum-catalyzed oxidation of alcohols is one of the oldest catalytic reactions, e.g., the catalytic effect of platinum on the aerobic oxidation of cinnamyl alcohol was described by Strecker in 1855 [7]. Supported noble metal catalysts are applied industrially in, *inter alia*, the oxidation of carbohydrates [8,9]. They will not be discussed further in this review since they are reviewed elsewhere in this special paper [10].

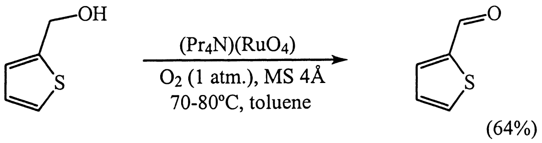
3. Oxidations with molecular oxygen: homogeneous catalysis

Most examples of aerobic oxidations of alcohols involve the use of group 8 metal complexes as catalysts. Especially ruthenium compounds, which are widely used as catalysts in organic synthesis [11], have been thoroughly investigated. For example, $RuCl_3$ and $RuCl_2(PPh_3)_3$ catalyze the oxidation of activated alcohols such as allylic alcohols, e.g., retinol, under mild conditions [12].



Aliphatic secondary alcohols similarly give the corresponding ketones albeit in relatively low conversions and selectivities [13]. Trinuclear ruthenium carboxylates, $Ru_3O(O_2CR)_6L_n$ ($L = H_2O$, PPh_3) are effective catalysts for the aerobic oxidation of lower aliphatic alcohols, i.e., ethanol, 1-propanol, isopropanol and 1-butanol [14] with activities approximately 10 times higher than those of $RuCl_3$ and $RuCl_2(PPh_3)_3$.

(n-Pr_4N)(RuO_4) was successfully used as a catalyst for the selective oxidation of alcohols with methylmorpholine N-oxide (NMO) as oxidant [2]. More recently, the same catalyst was also found to be highly efficient in the aerobic oxidation of alcohols [15]. A variety of primary and secondary alcohols such as aliphatic, allylic, benzylic and even sulfur/nitrogen-containing alcohols were selectively oxidized to the corresponding aldehydes and ketones.



Surprisingly, in combination with CuCl and 2-aminopyridine as base, this system is only capable of oxidizing benzylic and allylic alcohols [16].

Subsequently, Osborn and coworkers [17] reported that CuCl in combination with osmium tetroxide (OsO_4) and pyridine as base catalyzes the aerobic oxidation of primary allylic and benzylic alcohols to aldehydes at room temperature. This system, as well as (n-Pr_4N)(RuO_4)/O_2 and (n-Pr_4N)(RuO_4)–CuCl/O_2, gives a very dark reaction mixture suggesting the formation of colloidal material, i.e., these systems may involve heterogeneous catalysis. In the absence of other metals, CuCl in combination with 2,2′-bipyridine (bpy) as base/ligand also shows catalytic activity in aerobic oxidation of alcohols [18]. However, benzhydrol is the only suitable substrate and at least one equivalent of bpy (relative to substrate) is required to reach complete conversion. On the other hand, with *ortho*-phenanthroline as ligand $CuCl_2$ can catalyze the aerobic oxidation of a variety of primary and secondary alcohols to the corresponding carboxylic acids and ketones in alkaline media [19,20].

Ruthenium is widely used as a catalyst for hydrogen transfer reactions. These systems can be adapted to the aerobic oxidation of alcohols by employing oxygen and a catalytic amount of hydrogen acceptor in a multistep electron-transfer process (see Fig. 3). The low-valent ruthenium complex (1) reacts with the alcohol to give ruthenium dihydride (2), which undergoes hydrogen transfer to benzoquinone giving hydroquinone and (1). The reaction of hydroquinone with a second catalyst, $(ML_m)_{ox}$ (3), affords benzo-

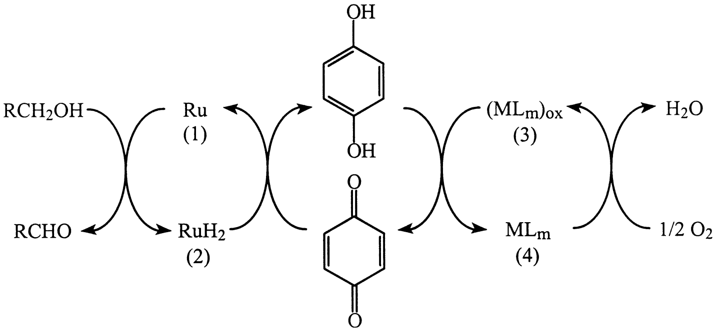
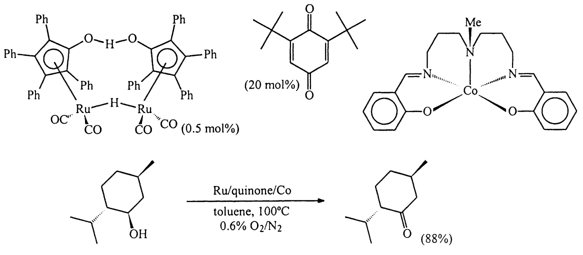


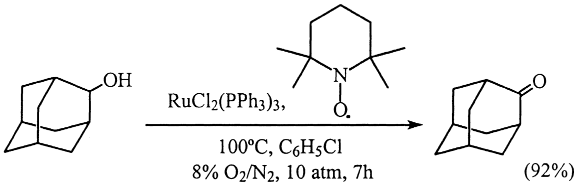
Fig. 3. Ruthenium catalyst in combination with a hydrogen acceptor for aerobic oxidations.

quinone and ML_m (4), and (3) is regenerated with molecular oxygen to complete the catalytic cycle.

A few catalytic systems based on this general concept have been described. For example, Bäckvall et al. [21] reported the $RuCl(OAc)(PPh_3)_3$/hydroquinone/Co(salophen)(PPh_3) system, which catalyzed the aerobic oxidation of benzylic and allylic alcohols. A few years later a modified Ru/quinone/Co system was published, which catalyzed the aerobic oxidation of secondary aliphatic alcohols, such as menthol [22].

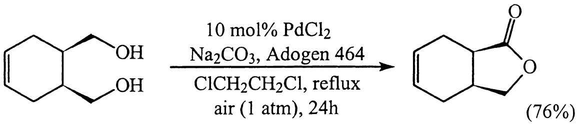


The regeneration of the quinone can also be performed directly with molecular oxygen, without the need for an extra catalyst, as shown by Ishii and coworkers [23]. A combination of $RuCl_2(PPh_3)_3$, hydroquinone and oxygen, in $PhCF_3$ as solvent, oxidized primary aliphatic, benzylic and allylic alcohols to their corresponding aldehydes in quantitative yields. We have used the free radical 2,2′,6,6′-tetramethylpiperidinyl-1-oxyl (TEMPO) as a cocatalyst. A combination of $RuCl_2(PPh_3)_3$ (1 mol%) and TEMPO (3 mol%) was remarkably effective for the aerobic oxidation of a variety of primary and secondary aliphatic alcohols, as well as benzylic and allylic alcohols, to give the corresponding aldehydes and ketones in >99% selectivities [24].



Surprisingly, the combination of CuCl (10 mol%) and (4-hydroxyl-)TEMPO (10 mol%) is only effective with benzylic and allylic alcohols [25].

A number of palladium-based systems are known, usually consisting of a palladium salt, such as $PdCl_2$ or $Pd(OAc)_2$, in combination with a base. In 1977, a $PdCl_2$–NaOAc system was reported for the aerobic oxidation of secondary alcohols under mild conditions in ethylene carbonate as solvent [26]. The same transformations can be catalyzed by $PdCl_2$ in combination with sodium carbonate (Na_2CO_3) and Adogen 464[1] as phase transfer catalyst [27], e.g., the aerobic oxidation of 1,4- and 1,5-diols gave lactone as the final product [28].



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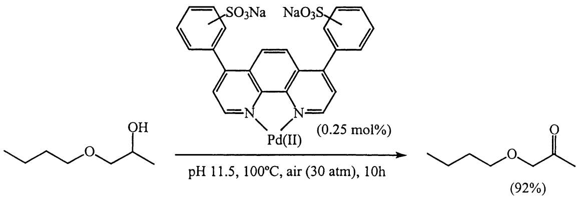
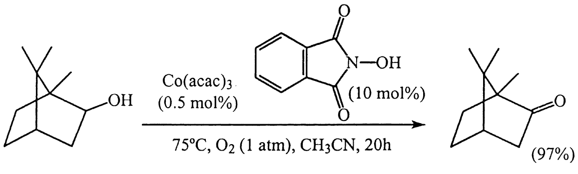
[1] Adogen 464 is a registered trademark of Ashland Chemical for methyltrialkyl(C_8–C_{10})-ammonium chloride.

$Pd(OAc)_2$ in combination with $NaHCO_3$ as base and DMSO as solvent catalyzed the aerobic oxidation of primary and secondary allylic and benzylic alcohols in fairly good yields [29]. Using pyridine/toluene instead of $NaHCO_3$/DMSO, primary and secondary aliphatic alcohols could also be oxidized [30]. A major shortcoming of these palladium-based systems is their relatively low activity; reactions typically require >12 h for completion with at least 5 mol% catalyst, i.e., TOF's ranging from one to three. Recently, we have described the aerobic oxidation of alcohols using a water soluble palladium(II) bathophenanthroline as a stable, recyclable catalyst [31].



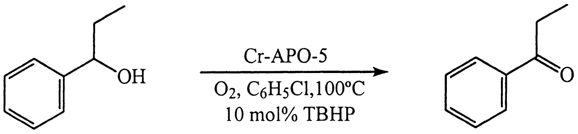
A wide range of alcohols were oxidized with TOF's ranging from 10 to 100, depending on the solubility of the alcohol in water. Primary alcohols afforded the corresponding carboxylic acids via further oxidation of the aldehyde intermediate. This is the first example of homogeneous catalytic aerobic oxidation of alcohols — activated or non-activated — in aqueous media.

Besides ruthenium and palladium, cobalt has proven to be an effective catalyst for aerobic oxidation of alcohols. $Co(acac)_3$ in combination with *N*-hydroxyphthalimide (NHPI) as cocatalyst catalyzes the aerobic oxidation of primary and secondary alcohols, e.g., borneol, to the corresponding carboxylic acids and ketones [32].



This reaction probably involves a free radical mechanism by analogy with other oxidations involving the Co/NHPI catalyst [33–35].

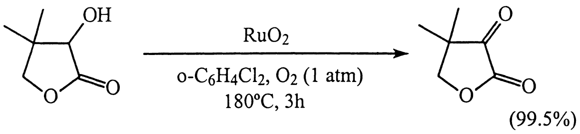
Besides cobalt, chromium also oxidizes alcohols via a free radical mechanism. Redox molecular sieves with chromium incorporated, and in particular Cr-APO-5, are effective catalysts for the oxidation of secondary alcohols with molecular oxygen [36].



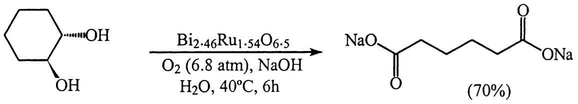
Although, this catalyst was first thought to be heterogeneous, extensive investigations have shown that the material is not stable toward leaching and that actually a homogeneous reaction is taking place in the liquid phase [37].

4. Molecular oxygen as oxidant: heterogeneous catalysis

Analogous to the homogeneous catalyst systems discussed above, many heterogeneous catalysts are based on ruthenium and both ruthenium metal and oxoruthenium species are capable of catalyzing aerobic oxidation of alcohols. For example, both RuO_2 and Ru/C (5 wt.% loading) catalyze the aerobic oxidation of activated alcohols such as allylic alcohols [38] and α-ketols [39].

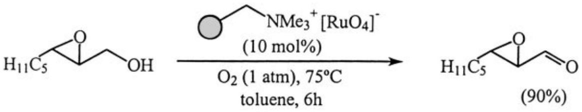


Besides carbon (C), cerium dioxide (CeO_2) can also be used as support [40]. Using the Ru/CeO_2 system, primary and secondary alcohols are smoothly converted to their corresponding aldehydes, acids and ketones at elevated temperatures (>140°C). Allylic alcohols, e.g., geraniol, and some cyclic alcohols, e.g., menthol, are unreactive. Vicinal diols, e.g., 1,2-cyclohexanediol, undergo aerobic oxidative cleavage forming dicarboxylic acids when heated together with a ruthenium pyrochlore oxide catalyst, $[A_{2+x}Ru_{2-x}O_{7-y}]$ (A = Pb, Bi; $0 < x < 1$; $0 < y < 0.5$), under high oxygen pressure in water at alkaline pH [41,42].



Besides ruthenium pyrochlore oxides, ruthenium-hydrotalcites form a second group of mixed oxide catalysts. These layered materials consist of a cationic Brucite layer with anionic compounds in the interlayer [43]. Various metals can be introduced in the Brucite layer and recently hydrotalcites having Ru in the Brucite layer — with the general formula $M_6Al_2Ru_{0.5}(OH)_{16}CO_3$ (M = Mg, Co, Mn, Fe, Zn) — have been reported [44,45]. These materials were shown to catalyze the aerobic oxidation of allylic, benzylic and heterocyclic alcohols in good yields. In contrast, the oxidation of secondary aliphatic alcohols was possible only with Ru/Co-hydrotalcite. In contrast to some homogeneous ruthenium catalysts, primary aliphatic alcohols are barely oxidized to aldehydes or carboxylic acids using the ruthenium-hydrotalcites as catalyst.

An alternative approach to immobilizing homogeneous catalysts is by attachment to a support. A good example of this is the polymer supported perruthenate (PSP), in which the polymer is Amberlyst A-26 [46]. Like the homogeneous analogue, PSP is capable of oxidizing a variety of alcohols, e.g., 2,3-epoxy-1-octanol.



However, the activity of PSP in the aerobic oxidation of alcohols is at least four times lower than that of the homogeneous analogue. Although it was mentioned that recycling of the catalyst can be performed by simple filtration, no recycling experiments are reported.

Similarly, polymer-anchored Ru(III)salen complex was synthesized by sequential attachment of ethylenediamine, salicylaldehyde and rutheniumtrichloride to a chloromethylated styrene–divinylbenzene copolymer with 8% cross-linking (Fig. 4) [47]. The activity of this catalyst in the aerobic oxidation of benzyl alcohol was ca. 75 times higher than that of the homogeneous [Ru(III)salenCl] analogue. However, recycling of the catalyst leads to a significant loss of activity (ca. 35%), because of leaching of ruthenium during catalysis.

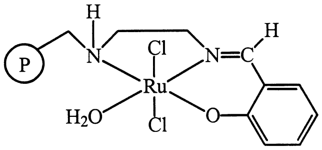
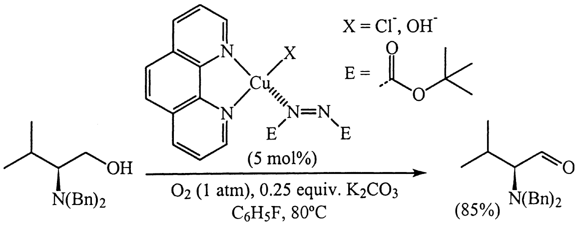


Fig. 4. A polymer-anchored ruthenium(III)salen complex.

A combination of CuCl, phenanthroline (phen) and di-*tert*-butylazodicarboxylate (DBAD), is capable of aerobically oxidizing a variety of alcohols to aldehydes and ketones in toluene in the presence of two equivalents of K_2CO_3 (relative to substrate) [48,49]. This contrasts with the reported homogeneous Cu-based systems, e.g., CuCl in combination with $(n\text{-}Pr_4N)(RuO_4)$ [16], OsO_4 [17] or TEMPO [25], where the scope is limited to allylic and benzylic alcohols. The oxidation using the CuCl/phen/DBAD-based heterogeneous catalyst mentioned above proceeds via hydrogen transfer from the alcohol via DBAD to molecular oxygen, as in the case of Ru/quinone/Co systems [21,22]. The K_2CO_3 acts as a support, as a base and as a water scavenger. In its absence, no oxidation is observed and in the presence of a catalytic amount, only low conversions are obtained. On the other hand, the amount of K_2CO_3 could be decreased from 2 to 0.25 equivalents (relative to substrate) without loss of catalytic activity by changing the solvent to fluorobenzene [50].

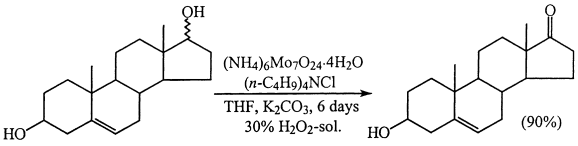


5. Hydrogen peroxide as oxidant: homogeneous catalysis

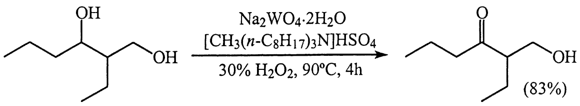
In the aerobic oxidations discussed in Section 4, the most effective catalysts are late transition elements, such as Ru and Pd, that operate via oxometal or hydridometal mechanisms. In contrast, the most effective catalysts with hydrogen peroxide as the oxidant are early transition metal ions with a d^0 configuration, e.g., Mo(VI), W(VI) and Re(VII), that operate via a peroxometal mechanism. Ruthenium compounds are generally not effective with H_2O_2 because they display high catalase activity, i.e., they catalyze rapid decomposition of H_2O_2. Early transition metal ions in high oxidation states, on the other hand, are poor catalysts for H_2O_2 decomposition.

One of the few examples of ruthenium-based systems is the $RuCl_3{\cdot}3H_2O$/didecyldimethyl-ammonium bromide (DDAB) reported by Sasson and coworkers [51]. This system catalyzes the selective oxidation of a variety of alcohols at high substrate: $RuCl_3$ (625:1) ratio in an aqueous/organic biphasic system. However, three or six equivalents of H_2O_2 were required, reflecting the propensity of ruthenium for catalyzing H_2O_2 decomposition.

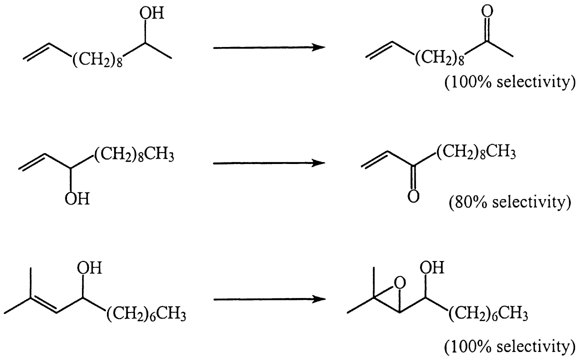
Several molybdenum- and tungsten-based catalysts, e.g., Na_2WO_4 and Na_2MoO_4 [52–54] and peroxo complexes of Mo and W [55] were reported to be effective in the oxidation of alcohols with H_2O_2. Similarly, ammonium molybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ in combination with a phase transfer catalyst, $(n\text{-}C_4H_9)_4NCl$, and a base (K_2CO_3) catalyzed the selective oxidation of secondary alcohols with H_2O_2 [56]. Interestingly, a more hindered alcohol moiety was selectively oxidized in the presence of a less hindered one.



Molybdenum- and tungsten-containing heteropolyanions are also effective catalysts for alcohol oxidations with H_2O_2 [57–59]. More recently, Noyori and coworkers [53,54] have achieved substantial improvements in the sodium tungstate-based, biphasic system first described by the group of Di Furia and Modena. By employing a phase transfer agent containing a lipophilic cation and bisulfate as the anion, e.g. $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, they obtained a highly active catalyst which is effective under solvent-free conditions and with only 1.1 equivalents of H_2O_2. For example, 1-phenylethanol was selectively oxidized to acetophenone with turnovers up to 180 000 [53,54]. As with all W- and Mo-based systems, the Noyori system shows a marked preference for secondary alcohols, e.g., 2-ethyl-1,3-hexanediol.



This system also catalyzed the chemoselective oxidation of unsaturated alcohols, e.g., 11-dodecen-2-ol, 1-dodecen-3-ol and 2-methyl-2-undecen-4-ol [53,54].



For allylic alcohols the selectivity depended on the number of substituents on the olefinic bond. Oxidation of 1-dodecen-3-ol, an allylic alcohol with a terminal olefinic bond, yielded the desired 1-dodecen-3-one in 80% yield, contaminated with 1,2-epoxydodecan-3-ol (14%) and 1,2-epoxydodecan-3-one (4%). On the other hand, 2-methyl-2-undecen-4-ol possessing a trisubstituted C=C bond underwent selective epoxidation to 2-methyl-2,3-epoxyundecen-4-ol.

Methyltrioxorhenium, $MeReO_3$ (MTO), also catalyzes the oxidation of alcohols with H_2O_2 via a peroxometal mechanism [60,61]. Primary benzylic and secondary aliphatic alcohols afforded the corresponding aldehydes and ketones, respectively, using two equivalents of H_2O_2. In the presence of bromide ion as a cocatalyst the reaction rate was increased by a factor of 1000 [61]. In this case the active oxidant may be hypobromite (HOBr), formed by MTO-catalyzed oxidation of bromide ion by H_2O_2.

Table 1
Oxidation of alcohols with Ti-sieves and hydrogen peroxide

Substrate	Catalyst	Time (h)	Alcohol conversion (%)	Selectivity of H_2O_2 (%)	Reference
Methanol	TS-1	8.5	50	87	[65]
1-Octanol	TS-1	3	50	100	[65]
Cyclohexanol	Ti-beta	3	44	55	[66]
Cyclooctanol	Ti-beta	3	48	61	[66]
3-Methylcyclohexanol	Ti-beta	3	7.3	11	[66]

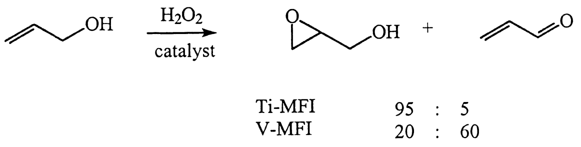
6. Hydrogen peroxide as oxidant: heterogeneous catalysis

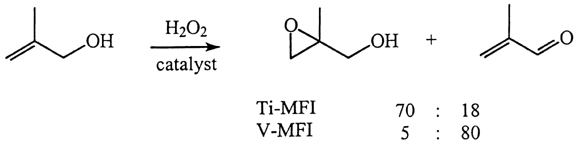
Analogous to the homogeneous systems discussed above, heterogeneous catalysts for the oxidation of alcohols with H_2O_2 generally involve early transition metals with a d^0 configuration. However, in contrast with homogeneous catalysis, where molybdenum(VI) and tungsten(VI) compounds were the most effective, the superior heterogeneous catalysts tend to be based on titanium(IV). The reason for this is that the corresponding heterogeneous catalysts based on Mo, W, Cr, V, etc. are susceptible to leaching under the reaction conditions [37]. Hence, examples of heterogeneous catalysts based on these elements may actually involve homogeneous catalysis.

One of the major discoveries in heterogeneous oxidation reactions employing hydrogen peroxide as the oxidant in the last decade was the discovery of titanium-silicalite (TS-1) [62,63], which is an isomorphously substituted molecular sieve and the progenitor of the so-called redox molecular sieves [64]. The discovery of its excellent oxidation activity, with 30% aqueous hydrogen peroxide as the oxidant, stimulated the extensive studies of redox molecular sieves as heterogeneous catalysts for liquid phase oxidations. A major reason for the enhanced activity of TS-1 is that the hydrophobicity of the framework stimulates the adsorption of the relatively hydrophobic substrates and hydrogen peroxide from an aqueous medium [37]. Alcohols such as methanol have been typically applied as solvents in epoxidation reactions catalyzed by TS-1, implying that they are unreactive. However, aliphatic alcohols display a moderate reactivity towards oxidation by H_2O_2 in the presence of Ti-molecular sieves as catalysts, e.g., as reported by Maspero and Romano for TS-1 [65].

The scope of alcoholic substrates is limited, however, because of the restricted size in TS-1 of 5.4 × 5.6 Å. The development of Ti-molecular sieves with larger pores, such as Ti-beta and mesoporous materials such as Ti-MCM-41, could overcome these limitations. Some activities for TS-1 and Ti-beta [66] for selected alcohols are collated in Table 1.

With allylic alcohols reaction with H_2O_2, in the presence of TS-1 or Ti-beta, generally gives high selectivities for epoxidation [67], rather than oxidation of the alcohol moiety. In contrast vanadium-containing molecular sieves have been reported to favor oxidation of the alcohol group in allylic alcohols. Thus, different chemoselectivities were observed in the oxidation of allylic and methallylic alcohols with H_2O_2 in the presence of TS-1 or VS-1 [68]. The titanium catalyst gave mainly epoxidation of the double bond whereas the vanadium catalyst favored oxidation of the alcohol moiety.





However, as we have noted elsewhere [37], in the case of vanadium-containing molecular sieves the observed catalysis is probably homogeneous in nature. Thus, vanadium sieves have been shown to be unstable towards leaching by H_2O_2 [37,69].

A zeolite-encapsulated vanadium picolinate complex was shown to be an effective catalyst for the oxidation of cyclohexanol and 2-propanol, using a hydrogen peroxide–urea adduct as the oxidant [70]. However, as was shown by the authors themselves, the observed catalysis was probably homogeneous in nature.

Similarly, vanadium-pillared montmorillonite (VPILC) was reported to catalyze the oxidation of benzylic alcohols with 30% H_2O_2 [71]. Interestingly, *para*-substituted benzylic alcohols were selectively oxidized in the presence of their *ortho*-isomers, suggesting a molecular sieve effect. However, no reactions were performed with homogeneous vanadium for comparison and here again, based on the experience gleaned from studies of analogous reactions with vanadium-substituted molecular sieves, we consider it highly likely that the observed activity is due to leached vanadium.

7. Concluding remarks

Increasingly stringent environmental regulations have provided the driving force for the development of clean catalytic methodologies for the oxidation of alcohols with O_2 and H_2O_2. Many of these methods appear to have broad synthetic utility but from the viewpoint of activity there is still room for improvement in many cases, i.e., turnover frequencies are of the order of $10\,h^{-1}$ or less. Nonetheless, we expect that such catalytic methodologies will be widely applied in the fine chemical industry in the future.

For industrial use heterogeneous catalysts are probably preferred, for their facile recycling, but in many cases heterogeneous counterparts to homogeneous catalysts are not stable towards leaching under oxidizing conditions. An important challenge for the future is to develop heterogeneous catalysts that are not only versatile, active and selective but also stable and recyclable.

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