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Polyaniline supported vanadium catalyzed aerobic oxidation of alcohols to aldehydes and ketones

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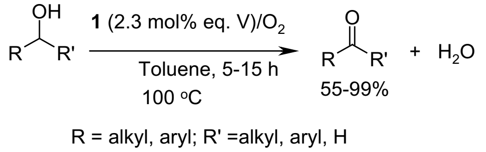
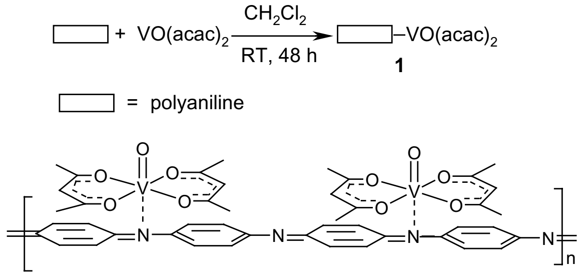
Abstract—Polyaniline supported vanadium complex **1** catalyzes efficiently the oxidation of alcohols to aldehydes and ketones in high yields under molecular oxygen in toluene at ca. 100 °C. The catalyst **1** can be recycled without loss of activity.

The oxidation of alcohols to aldehydes and ketones is one of the most important and frequently used functional group transformations in organic chemistry.[1] Several methods and reagents have been developed for this purpose. Most of these oxidizing reagents are, however, often needed in stoichiometric quantities and the work up procedures are laborious.[2] Thus, from the standpoint of atom economy for chemical reactions, much attention has been focused recently on developing catalytic systems with molecular oxygen as the primary oxidant in the presence of transition metal catalysts[3–15] and awaits further discovery of new methods especially in the absence of additives. Recently, we reported that V_2O_5 catalyzes the oxidation of alcohols to aldehydes and ketones by atmospheric oxygen.[6d] In this procedure, the oxidation of primary alcohols to aldehydes operates in the presence of base; in its absence esters are obtained. This is due to the acidic nature of the reaction medium that favors the formation of a hemiacetal followed by oxidation to esters. During the course of our studies on the oxidation of organic compounds,[16] we found that polyaniline supported $VO(acac)_2$ **1** catalyzes efficiently the oxidation of alcohols to aldehydes and ketones in high yields with molecular oxygen. This protocol does not require base and the catalyst **1** can be recycled without loss of activity (Scheme 1).



Scheme 1.

The catalyst **1** was prepared[17] by stirring a 1:1 (by weight) mixture of $VO(acac)_2$[18] and polyaniline in dichloromethane at room temperature for 48 h and a tentative structure is shown in Figure 1.[19] After UV–vis and IR characterization,[20] catalyst **1** was investigated for the oxidation of benzyl alcohol under molecular oxygen in acetonitrile, toluene and *p*-xylene as solvents at 80 °C for 15 h. As expected oxidation took place and afforded benzaldehyde in 68%, 91% and 45% yields, respectively. Alternatively, the reaction could be driven to completion to give a 98% yield of benzaldehyde by stirring the reaction mixture at ca. 100 °C in toluene for 9 h.[21] No further oxidation of the aldehyde to benzoic acid was observed under these conditions, whereas the



1

Figure 1. Proposed polyaniline supported $VO(acac)_2$ structure.

Keywords: Oxidation; Alcohol; Aerobic; Vanadium; Supported catalyst.

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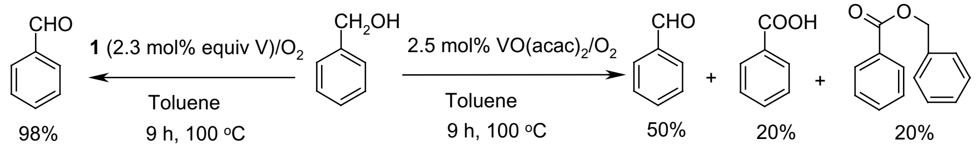
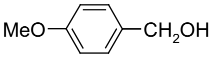
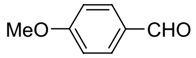
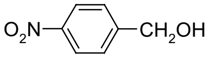
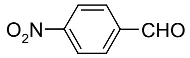
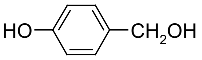
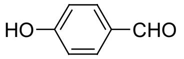
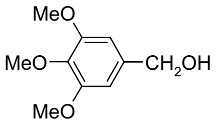
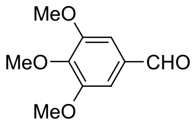
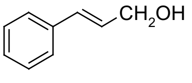
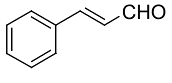
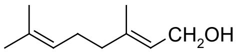
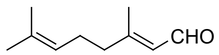
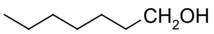
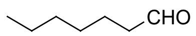
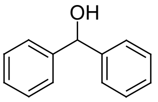
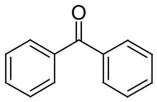
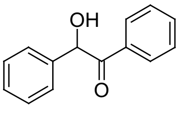
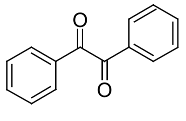
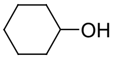
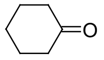
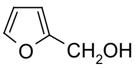
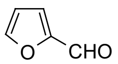
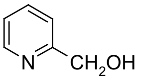
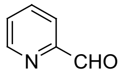


Scheme 2.

oxidation of benzyl alcohol using $VO(acac)_2$ was less selective and provided a 1:1:2.5 mixture of benzoic acid, benzyl benzoate and benzaldehyde in a 90% combined yield (Scheme 2).

To evaluate the scope of this catalytic system, the oxidation of other aromatic and aliphatic alcohols was studied (Table 1, entries 1–12).[21] Substrates having both electron donating and electron withdrawing groups in the aromatic ring, 4-methoxy-, 4-nitro-, 4-hydroxy- and 3,4,5-trimethoxy-benzyl alcohols, were oxidized to the corresponding aldehydes in high yields. A similar reactivity was observed with the allylic alcohols, geraniol and cinnamyl alcohol. The saturated alcohol, heptan-1-ol was less reactive, while secondary alcohols, diphenylmethanol, benzoin and cyclohexanol provided the corresponding ketones in quantitative yields. Likewise, furfurol and pyridine-2-methanol could be oxidized to the respective aldehydes in high yields. No oxidation was observed at a phenolic OH, the N-atom of pyridine-2-methanol and the carbon–carbon double bond of the allylic alcohols.

Table 1. Aerobic oxidation of alcohols to aldehydes and ketones with catalyst **1**[a]

Entry	Alcohol	Time (h)	Product	Yield (%)[b]
1		9		95
2		15		78
3		9		96
4		9		97
5		7		98
6		9		85
7		15		55[c]
8		5		>99
9		5		>99
10		7		>99
11		9		92
12		12		88

The identity of the compounds was ascertained by NMR (^1H and ^{13}C) and IR spectra and by comparison with authentic samples.

[a] Catalyst **1** (20 mg, 2.3 mol% equiv V) and the substrate (1 mmol) were stirred in toluene (3 mL) at ca. 100 °C under an oxygen balloon.

[b] Isolated yield.

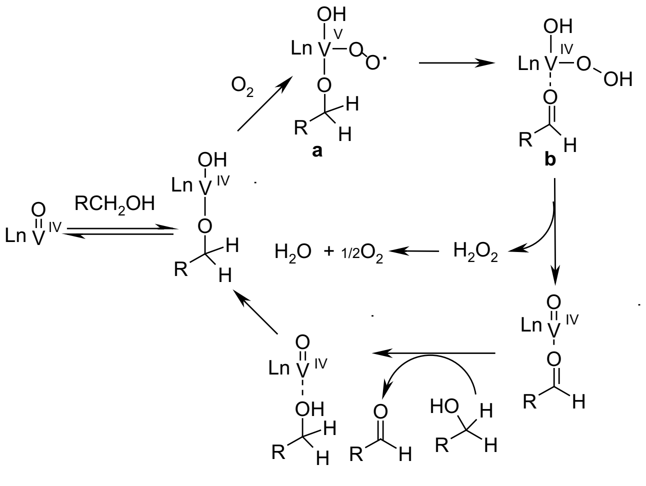
[c] 40 mg of **1** used.

Table 2. Recycling **1** for the aerobic oxidation of benzyl alcohol to benzaldehyde

Run[a]	PhCHO (%, yield)[b]	Recovery **1** (%)
1	98	99
2	96	96
3	93	94

[a] Benzyl alcohol (1 mmol) and complex **1** (20 mg for 1st run) were stirred under an oxygen balloon in toluene (3 mL) at ca. 100 °C for 9 h.

[b] Determined by GC.



Scheme 3.

The formation of a mixture of an aldehyde, carboxylic acid and ester in the homogeneous process may be due to the acidic nature of the reaction medium ($pH = 4.3$), which can facilitate the formation of a hemiacetal followed by oxidation to the ester (Scheme 2).[6d] Such a functional transformation does not take place in the case of the heterogeneous process because its pH is 6.6.

The catalyst **1** can be filtered and recycled without loss of activity (Table 2). Regarding the mechanism, a catalytic cycle is proposed in Scheme 3. The alcohol followed by molecular oxygen may coordinate with the catalyst **1** to provide the superoxo complex **a** that can readily undergo intramolecular hydrogen abstraction to give the intermediate **b** and elimination of H_2O_2 to complete the catalytic cycle.

In conclusion, an oxidation of alcohols to aldehydes and ketones is described using a recyclable polyaniline supported vanadium catalyst **1** under molecular oxygen. The reactions are efficient, function in the absence of any additive and generate water as the only by-product.

Acknowledgements

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18. A 1:1 mixture of polyaniline (200 mg) and VO(acac)$_2$ (200 mg) was stirred in dichloromethane (15 mL) under atmospheric oxygen at room temperature for 48 h. The polyaniline supported VO(acac)$_2$ **1** was filtered and washed with dichloromethane until the filtrate was colorless. The catalyst **1** was then dried under vacuum to provide a black powder (322 mg). Concentration of the combined filtrate provided 75 mg of unsupported VO(acac)$_2$. Data for **1**: UV–vis (solid): λ_{max} 276, 327, 334, 383 nm. IR (KBr): 1593, 1501, 1306, 1148, 1025, 999, 943, 835 cm^{-1}.
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21. The alcohol (1 mmol) and catalyst **1** (20 mg, 2.3 mol% equiv V) were stirred under an oxygen balloon in toluene (3 mL) at ca. 100 °C for the appropriate time (see Table 1). The catalyst was filtered and the filtrate after GC analysis passed through a short pad of silica gel using a mixture of diethyl ether and hexane as eluent or distilled to provide the analytically pure carbonyl compound.