

# Alcohols Oxidation by oxygen $O_2$ in presence of vanadoheteropolyacid ( $H_5PMo_{10}V_2O_{40}$ ) as green catalyst

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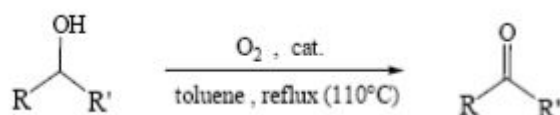
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**Abstract:** The catalytic oxidation of alcohols into relevant carbonyl compounds is economically and environmentally of interest. Various catalysts have been developed for these processes. In this regard, vanadoheteropolyacids because of high oxidant qualities concerning  $V^{5+}$  and high acid power are convenient. In this work a new method has been proposed for oxidation of alcohols using vanadoheteropoly acid ( $H_5PMo_{10}V_2O_{40}$ ) as catalyst under atmosphere ( $O_2$ ) as final stoichiometric oxidant. In this method the alcohol and the amount or percentage of catalytic of heteropolyacid in toluene solvent has been refluxed under oxygen atmosphere and correlated carbonyl compound was formed with high yield as the only product as showing in following.



The control experiments showed that reflux conditions  $O_2$  and hetero poly acid are necessary for this reaction. In this condition the benzylic alcohols type 1 and type 2 with different substitutions on the phenyl ring with suitable yield were oxidized to ketons and aldehydes without more oxidation into carboxylic acids.

**Key words:** heteropolyacid, catalyst, reflux, oxidation.

## Introduction

One of the research works of catalysts which has been largely developed in recent years is the examination of chemical properties and reactivity of cluster compounds of metal -oxygen named polyoxometalates.

The reasons of this consideration are factors such as physical and chemical variation of these compounds, simple preparation, the ability of adjustment of acid power with opposite ion changing or hetero atoms changing and simple recoverability of these catalysts through transforming into insoluble salts or placing them on the solid support [1, 2].

These advantages led to generation of extensive investigations for application of polyoxometalates not only in catalysis but also in the fields of analysis, medicine, electronic, protective coatings, photo catalysts, science of materials and micro technology. Another important field which is of interest in the catalysis studies for polyoxometalates has been the ability of these compounds in the oxidation of organic compounds and also the compounds with the lowest reactivity such as light alkanes[3, 4].

Many much articles have been published on the physical and chemical properties of these

compounds in different reactions [5]. An important class of cluster polyoxometalates in their acid or are called heteropolyacids (HPAs) which are formed by the metals groups V and VI including tungsten and molybdenum[6].

Catalysis by heteropolyacids and other polyoxometalates have important research fields which are developing heteropolyacids as catalysts which have various advantages that makes them interesting economically and environmentally. These compounds are the powerful Bronsted acids and classified as super acids [6].

In addition, the high and effective oxidant characteristic of these compounds allowed them to be able to capture some electrons reversible in redox reactions in the condition of moderate transformations[7,8], and through re-oxidation by oxidants such as  $O_2$ ,  $H_2O_2$  and even metal ions such as  $Ag^+$ ,  $Cu^{+2}$ ,  $Pt^{+2}$ , retain to initial state reversibility means that these compounds maintain their structure during electron exchange [9]. These compounds have homogeny catalysts selectivity and heterogenic catalysts stability.

### Experimental Method

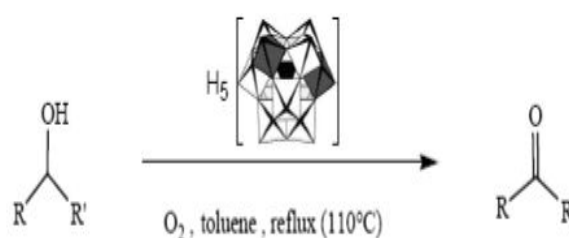
After synthesis of hetero poly acid  $H_5PMo_{10}V_2O_{40}$  the catalysis role of which in alcohols oxidation by oxygen has been examined. This way, in a two-head 100ml balloon containing a stirrer, 1m: mole alcohol and 100 mg catalyst  $H_5PMo_{10}V_2O_{40}$  and 10 ml toluene solvent have been put and it passed through a mixture of  $O_2$  gas for the duration of 5 minutes and the system was refluxed under an oxygen gas balloon. Reaction progress and pursuing the change in them, early identification of product type or products resulting from oxidation using thin-layer chromatography surfaces (TLC) having fluorescence indicators in (CF254)  $\lambda_{max} = 254 \text{ nm}$  made in merk company has been studied and examined. So in certain time interval TLC was done in reaction mixture. After the terminal confirmed by TLC, the product has been separated and purified by silica gel surface chromatography (ethyl acetate mix /  $CCl_4$ ). This product using one or more data TLC, mp, IR,  $^1H$ -NMR and GC-MS and comparing these data with the available data for commercial samples of these products have been identified in laboratory and their structure was defined. The products and their yield presented in table 1.

### Results and discussion

After some tests on some sample alcohols and assurance of the efficiency of the compound

$H_5PMo_{10}V_2O_{40}$  as catalyst in alcohol oxidation by oxygen, the oxidation of different alcohols in the presence of this catalyst in toluene solvent under reflux in oxygen atmosphere has been examined.

According to the general method earlier, the mixture of every alcohol with catalysis extent of  $H_5PMo_{10}V_2O_{40}$  refluxed in toluene solvent saturated with oxygen. After the completion of the reaction, the products were separated and using one or more physical and spectral data including TLC, melting point, IR, GC, MS and  $^1H$ -NMR have been identified. The data indicated that all alcohols are oxidized to carbonyl compounds according to the general reaction below.



The results are summarized in table 1. Studying the results in the table shows that compared to alcohol benzyl, the benzylic alcohols having electron donor groups such as *p*-iso-Pr, *p*-tert-Bu, *p*-MeO are more active to oxidation and product were generated in shorter time with high yield. On the other hand, the benzylic alcohols having acceptor groups such as  $NO_2$ ,  $CF_3$ , F on the phenyl ring have had low activities. Also the benzylic alcohols type 2 such as 1-phenyl alcohols and benzhydrol has been oxidized slower than the benzyl alcohols type i..

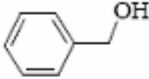
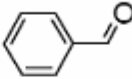
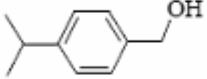
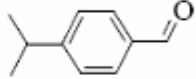
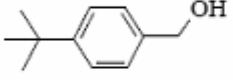
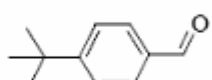
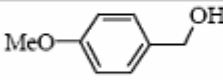
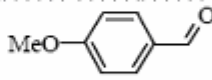
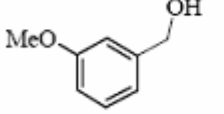
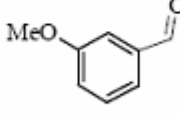
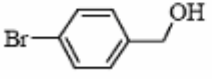
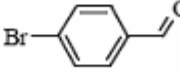
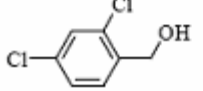
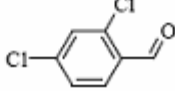
In addition allylic alcohol such as cinnamyl alcohol are selectively changed in to the relevant aldehyde without the inter mention of carbon- carbon double bond, and it indicates that the method mentioned above is to be an appropriate method for the oxidation of functional group OH in the presence of functional groups such as C=C.

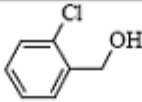
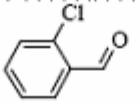
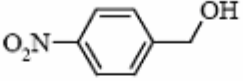
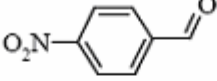
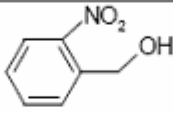
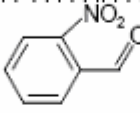
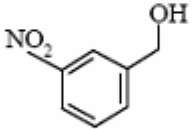
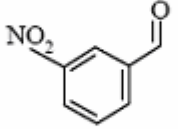
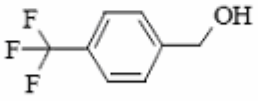
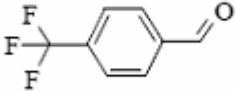
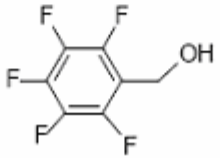
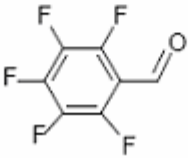
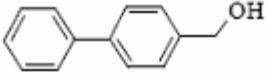
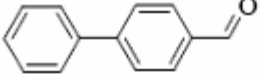
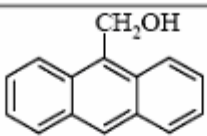
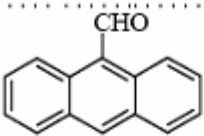
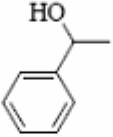
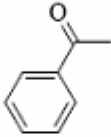
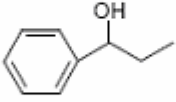
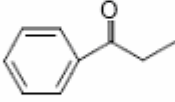
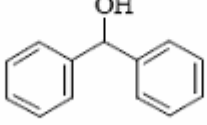
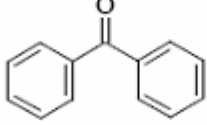
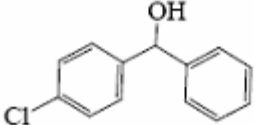
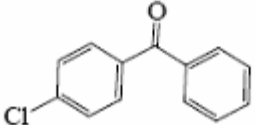
Under this oxidation, the hetero aromatic alcohols having atoms O, N and S in its aromatic rings have been examined. A study by TLC and also GC-MS suggested that these types of alcohols have been oxidized as well and turned into the relevant aldehydes.

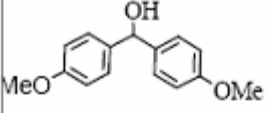
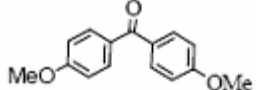
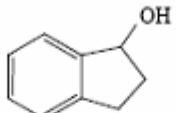
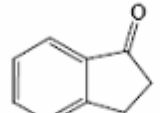
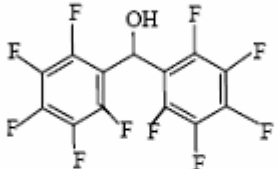
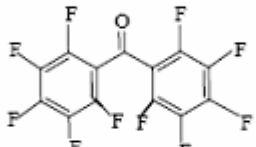
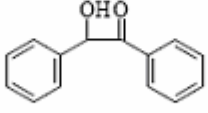
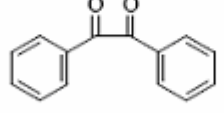
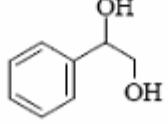
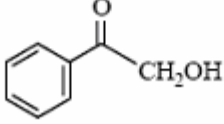
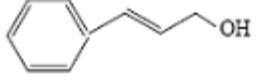
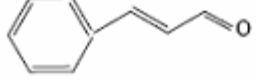
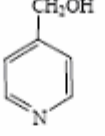
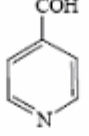
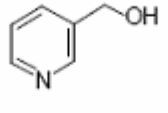
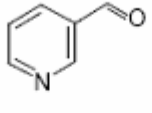
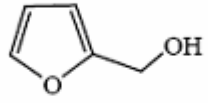
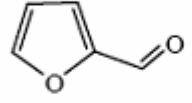
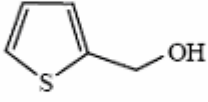
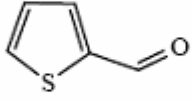
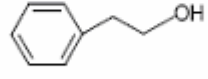
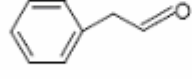
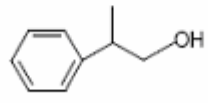
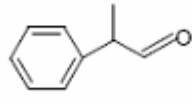
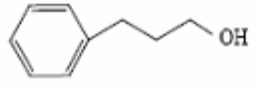
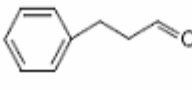
It can be seen from the table that the oxidant system is able to oxidize non-benzylic alcohols and Aliphatic, but in these cases the reaction time was longer. The study using TLC and GC-MS showed that these groups of alcohols are changed into carbonyl compounds, with high yield, as well.

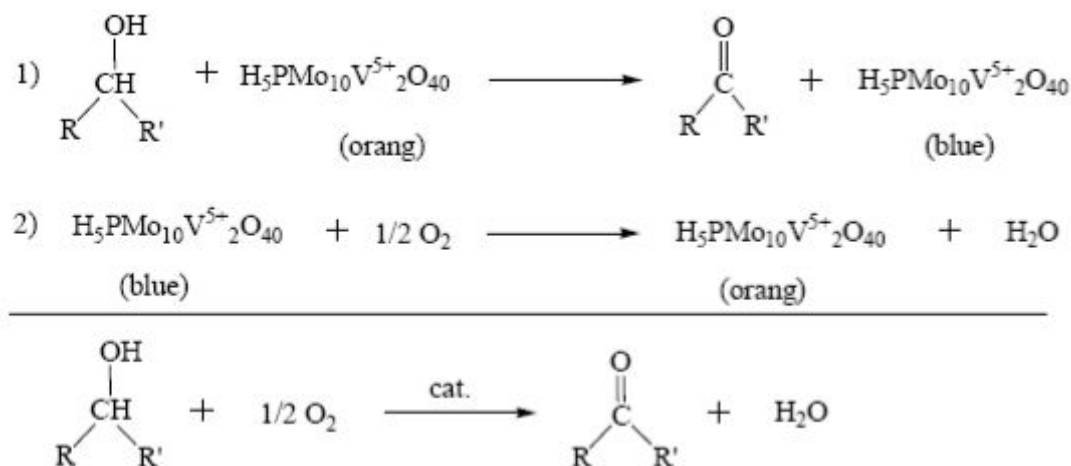
**Table- 1: The result of alcohols oxidation by O<sub>2</sub> using H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> as catalyst.**

$$\text{RR'CHOH} \xrightarrow[\text{toluene, reflux (110}^\circ\text{C)}]{\text{O}_2, \text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}} \text{RR'C=O}$$

number	alcohol	reactio time(h)	products	yield
1		2		90
2		1/25		96
3		1/25		95
4		1/25		94
5		1/5		86
6		1		95
7		1		94

8		1/25		90
9		5		95
10		5		60
11		4		82
12		4		82
13		5		85
14		2/5		75
15		2/5		80
16		2/5		90
17		2		95
18		2/5		90
19		2		92

20		1/5		85
21		2/5		90
22		5		70
23		3		90
24		1/5		92
25		1/5		88
26		6		70
27		6		66
28		6		78
29		6		70
30		4		84
31		4		82
32		4		65



Although lack of necessary facilities made the precise mechanism of the process unclear, regarding the evidence and observation resulted in this project and also reported data in scientific writing we can propose the possible methods [10]. The possible method for the oxidation of alcohols by oxygen in presence of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  as catalyst is possibly plausible through the two main stages suggested below and finally catalyst is regenerated in second stage.

The evidence confirming the possible method above is as follow:

A) Without the presence of oxygen and catalyst the new reaction is not plausible that much.

B) The presence of the catalytic object  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  suffices for doing the reaction, it means that these compounds have catalytic role.

C) During the reaction the color of the compound turns into blue which is an indication that, electron is transferred to  $\text{V}^{5+}$  from alcohol in the catalyst, and reduce to  $\text{V}^{4+}$ .

Based on the pattern of high activity of the types with electron giver groups can be due to low potential and thus feasibility of their oxidation by the  $\text{V}^{5+}$  ion present in catalyst. The better reactivity of benzylic alcohols compared to non-benzylic (Aliphatic) is due to the fact that the bond energy of benzylic CH link ( $\text{ArC(R)OH-H}$ ) is about 30 kJ/mol less than bond of Alkyl CH link ( $\text{R}_2\text{COH-H}$ ) and the former gives

more stable average by elimination of hydrogen. Therefore in the fields of competition, the benzylic condition is more easily oxidized. This can justify the selective oxidation in OH benzylic place in the presence of OH non-benzylic and thus the chemo selectivity of the reaction.

### Conclusion

Generally a selective, efficient and easy method has been offered for the oxidation of alcohols. This method can be a useful and interesting synthesis for chemists. This method which is a new chemical method has been carried out using vanado hetero poly acid ( $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ) which has high oxidant power, high acidic power, non-corroding, non-toxic and solid qualities.

In this procedure different kinds of type I and type II alcohols has been oxidized with or without the presence of taker or giver electrons groups in the system  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{O}_2/\Delta$  the benzylic alcohols with giver electron groups, compared to those of electron takers on the aromatic link, have more activities and has more yield in shorter time.

All alcohols including benzylic alcohols, non-benzylic alcohols and alcohols with hetero atom ring are oxidized, even though the benzylic alcohols have more activity.

## References

1. M.Heravi, F.K.Behbahani, R.Hekmatshoar and A.Oskooie, Catalytic synthesis of 2,3-dihydro-1H-1,5-benzodiazepines by ferric perchlorate, *Catal.Comm.*, 7 (2006),136
2. H.Firouzabadi, N.Iranpoor and K.Amani, Aldehyde synthesis by oxidation of alcohols and rearrangements, *Synthesis*, (2003) 408.
3. M.T.Pope, *Heteropoly and Isopoly anions*; Speriniger Verlay, New York (1983).
4. I.V.Kozhevenicov, *Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions*, *Chem.Rev.*, 89 (1998) 171.
5. I.V.Kozhevenicov, *Catalysis for Fine Chemical Synthesis*, *Catalysis by polyoxometalates 2*; Wiley; New York (2002).
6. K.K.Banerji, Kinetics and mechanism of the oxidation of phosphinic, phenylphosphinic, and phosphorous acids by pyridinium fluorotrioxochromate(VI), *J.Org.Chem.*, 53 (1988) 2154.
7. S.Tangestaninejad and B.Yadollahi, Oxidation of Hydrocarbons With Hydrogen Peroxide Catalyzed by Zinc Containing Polyoxometalate, *Chem.Lett.*, (1998) 511.
8. E.Ishikawa and T.Yamase, Kinetics of epoxidation of cyclooctene with  $H_2O_2$  by  $\alpha$ -Keggin  $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$  catalyst in cetonitrile, *J.Mol.Catal.A:Chem.*, 142 (1999) 61.
9. I.G.Kolesnik, E.G.Zhizhina and K.I.Matveev, Catalytic oxidation of 2,6-dialkylphenols to the corresponding 2,6-dialkyl-1,4-benzoquinones by molecular oxygen in the presence of P–Mo–V heteropoly acids, *J.Mol.Catal.A:Chem.*, 153 (2000) 147.
10. Craig L. Hill and Christina M. prosser-McCartha, Homogeneous catalysis by transition metal oxygen anion clusters, *Coord.Chem.Rev.*, 143 (1995) 407.

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