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Oxidation of benzylic alcohols with molecular oxygen catalyzed by $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$

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ABSTRACT

The aerobic oxidation of alcohols was efficiently completed in high conversion and selectivity using $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$ as catalyst under mild reaction condition. This reaction provides a new environmentally friendly rout to the conversion of alcoholic function to carbonyl groups.

*Keywords: Green chemistry; aerobic alcohol oxidation; polyoxometalates (POMs).*

1. Introduction

One of the major challenges in catalysis research is to design and develop selective oxidation catalysts that operate at mild conditions [1]. Oxidation of benzyl alcohol to benzaldehyde (without forming further oxidation products like benzoic acid) is an important organic transformation. This reaction is widely investigated as it provides chlorine-free benzaldehyde required in perfumery and pharmaceutical industries [2, 3]. Traditionally, this transformation is carried out using stoichiometric amounts of chromium and manganese reagents [4-6]. These oxidants are not only expensive but generate copious amounts of toxic heavy-metal waste. Much progress has been made to develop catalytic systems using molecular oxygen as the terminal oxidant [7]. Representative examples are the catalytic systems using transition metal catalysts [8-16] or stable nitroxyl free radicals (TEMPO) [17]. Therefore, developing green, selective and efficient aerobic catalysts for the oxidation of alcohols, that can use air or pure oxygen (O_2) as oxidant, is of paramount importance for both economic and environmental reasons [18].

Polyoxometalates (POMs) constitute a diverse class of inorganic oxo-metal clusters composed of early transition metals in their highest oxidation state [19]. They have tunable acidic and redox properties that can be controlled by changing the constituent elements. The use of POMs as oxidation catalysts has attracted attention because unlike organic porphyrins which tend to oxidize and degrade after a few catalytic cycles, POMs resist oxidation due to presence of W or Mo atoms in their highest oxidation state [20-34].

The salts of these POMs, which are more thermally stable than their parent acids, are also extensively used as catalysts to obviate solubility problems during reactions The exchange of the protons in the $H_3PMo_{12}O_{40}$ with a metal on changes the system from an acidic one to neutral one. The deposition of POMs on solid supports is important for catalytic applications, as the surface areas of unsupported ones are low. Herein, we wish to report a simple, clean, efficient, and eco-friendly process for the oxidation of benzylic alcohols with molecular oxygen catalyzed by $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$ (Scheme1).

$$ArCH_2OH \xrightarrow[O_2, CH_3CN, reflux]{Cu_{3/2}PMo_{12}O_{40}/SiO_2} ArCHO$$

1a-1t → **2a-2t**
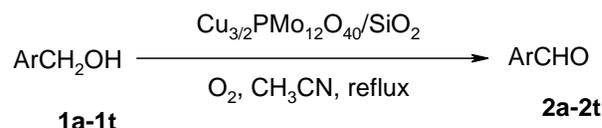
Scheme 1.

2. Experimental

All materials were commercial reagent grade. $H_3PMo_{12}O_{40}$ were purchased from Merck chemical company. FT-IR spectra were obtained as potassium bromide pellets in the range 400-4000 cm^{-1} with Nicolet *Impact 400 D*. ^1H NMR spectra were recorded with a Bruker-Avance AQS 300 MHZ. The melting points were determined using an electrothermal digital melting point apparatus and are uncorrected. Reaction courses and product mixtures were monitored by thin layer chromatography.
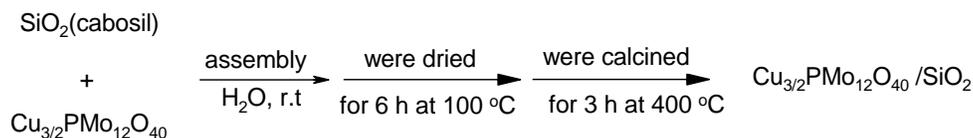
2.1 Preparation of 35 % $Cu_{3/2}PMo_{12}O_{40}/SiO_2$

$Cu_{3/2}PMo_{12}O_{40}/SiO_2$ was prepared by method of incipient wetness. In a typical process, a 560 mg portion of $Cu_{3/2}PMo_{12}O_{40}$ was dissolved in deionized water and impregnated drop wise into 1600 mg SiO_2 (Cabosil) in 25 ml methanol, with constant agitation. The resulting pastes were dried for 6 h at 100 °C and calcined for 3 h at 400 °C (Scheme 2).

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SiO_2(cabosil)

+

$Cu_{3/2}PMo_{12}O_{40}$

→ assembly H_2O, r.t → were dried for 6 h at 100 °C → were calcined for 3 h at 400 °C → $Cu_{3/2}PMo_{12}O_{40}$ /SiO$_2$

Scheme 2. Preparation of $Cu_{3/2}PMo_{12}O_{40}$
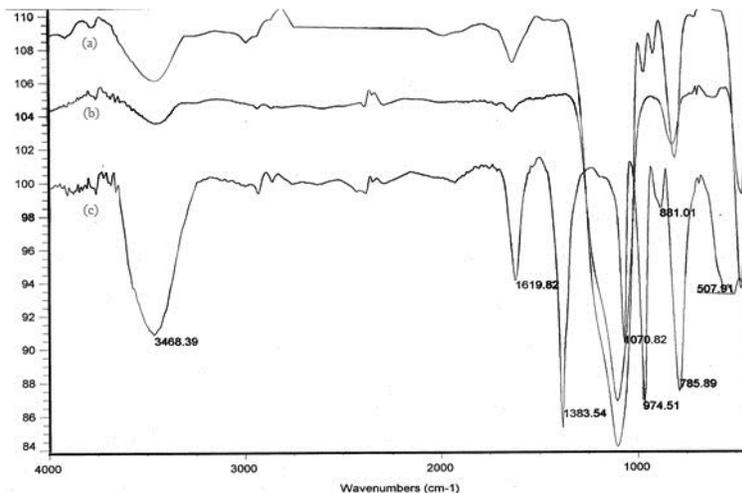
Fig. 1. FT-IR spectra of (a) 35 % $Cu_{3/2}PMo_{12}O_{40}/SiO_2$, (b) pure SiO_2(cabosil), (c) pure $Cu_{3/2}PMo_{12}O_{40}$.

3. Results and Discussion

3.1. Catalysts characterization

The physicochemical properties of supported POM catalysts by XRD, FT-IR and neutron activation analysis (NAA) demonstrated that POM were anchored on the surface of supports and POM still remained the Keggin structures**.** FT-IR spectra have been proven to be a powerful technique for study of surface interaction between HPA and organic and inorganic supports. Fig. 1 represents the FT-IR transmission spectra of pure SiO_2, pure $Cu_{3/2}PMo_{12}O_{40}$ and supported $Cu_{3/2}PMo_{12}O_{40}$ catalysts calcined at 400 °C for 3h. It shows a typical infrared spectrum of silica [35] with bands assigned at 1626 and 821 cm^{-1} together with a broad band at 1106 cm^{-1} (Fig.1b). The spectrum of pure $Cu_{3/2}PMo_{12}O_{40}$ shows four bands in the range 1250–500 cm^{-1}. These bands are assigned at 1070, 966, 881 and 785 cm^{-1}, which are the characteristic bands of the Keggin structure (Fig.1c). These were assigned [36, 37] to v_{as}(P–Oa), v_{as}(Mo–Oa), v_{as}(Mo–O–Mo) and v_{as}(Mo–Oc–Mo), respectively. In addition, the observed band at 595 cm^{-1} may be attributed to the δ (P–O) vibration [36]. Moreover, the band located at 1619 cm^{-1} may be characteristic the O–H stretching vibration. The FT-IR spectrum of $Cu_{3/2}PMo_{12}O_{40}$ /SiO$_2$ indicates that most of characteristic bands of the parent Keggin structure, could be found in HPA fingerprint region (1250–500 cm^{-1}), are not shown or appeared in the same assignable position of the bands correspond to SiO$_2$ host material (Fig.1a). Fig. 2a shows the XRD patterns of 35 % $Cu_{3/2}PMo_{12}O_{40}/SiO_2$ within the 2θ range of 5–70°. The peaks corresponding to amorphous 35 % $Cu_{3/2}PMo_{12}O_{40}/SiO_2$ are present. No peaks from any crystalline form of $Cu_{3/2}PMo_{12}O_{40}$ could be observed, indicating that $Cu_{3/2}PMo_{12}O_{40}$ was inserted into SiO$_2$ matrix.

3.2. Oxidation of Benzylic Alcohols Catalyzed by $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$

The influence of the various solvent on the yield of the reaction was investigated using of benzyl alcohol as the substrate (Table 1).From these studies it was deduced that acetonitril to be the most favorable solvent.

To begin the oxidation of benzyl alcohol was examined as a standard substrate in the presence of a 0.4g catalyst in CH_3CN under O_2 pressure. The oxidation took place affording benzaldehyde in 90% yield when the reaction mixture was allowed to stir at 83°C for 70 min.

To study the scope of this procedure the oxidation of other alcohols was next studied (Table2 entries 2-20). All benzylic alcohols having

Table 1

Effect of solvent on the yield of the synthesis of benzyldeyde.[a]

Entry	Solvent	Time(min)	Yield (%)[b]
1	CH_3CN	70	90
2	*n*-hexane	120	45
3	H_2O	120	30
4	CH_2Cl_2	120	50
5	CH_3OH	120	35
6	$(C_2H_5)_2O$	120	30

[a]Reaction conditions: benzyl alcohol (108 mg, 1 mmol), catalyst (0.4 g), solvent (3 ml), reflux, O_2 pressure.

[b]Isolated yield.

Table 2

Oxidation of benzylic alcohols with O_2 catalyzed by $Cu_{3/2}[PMO_{12}O_{40}]$ /SiO_2 in CH_3CN.[a]

Entry	Substrate (**1**)	Ar or Alcohols	Product (**2**)	Time (min)	Yield (%)[b]
1	a	C_6H_5	a	70	90
2	b	$4\text{-}NO_2\text{-}C_6H_4$	b	120	90
3	c	$3\text{-}NO_2\text{-}C_6H_4$	c	120	80
4	d	$2\text{-}NO_2\text{-}C_6H_4$	d	120	75
5	e	$4\text{-}HO\text{-}C_6H_4$	e	75	95
6	f	$2\text{-}HO\text{-}C_6H_4$	f	100	81
7	g	$4\text{-}Cl\text{-}C_6H_4$	g	90	90
8	h	$2\text{-}Cl\text{-}C_6H_4$	h	100	78
9	i	$4\text{-}MeO\text{-}C_6H_4$	i	60	88
10	j	$3\text{-}MeO\text{-}C_6H_4$	j	100	85
11	k	$4\text{-}F\text{-}C_6H_4$	k	90	83
12	l	$4\text{-}Br\text{-}C_6H_4$	l	100	85
13	m	$4\text{-}Me\text{-}C_6H_4$	m	80	85
14	n	$3\text{-}Me\text{-}C_6H_4$	n	100	84
15	o	$2\text{-}NH_2\text{-}C_6H_4$	o	120	80
16	p	2-Thienyl	p	90	87
17	q	$2\text{-}Me\text{-}C_6H_4$	q	90	80
18	r	2-Pyridyl	r	90	85
19	s	1-phenyl ethanol	s	75	65
20	t	$C_6H_5CH_2$	t	75	85
21	a	C_6H_5	a	120	50[c]
22	a	C_6H_5	a	120	55[d]

[a] Reaction conditions: benzylic alcohol (1 mmol), catalyst (0.4 g), CH_3CN (3 ml), reflux, O_2 pressure.

[b] Isolated yield; All products were identified by comparsion with authentic sample (mp, IR, NMR).

[c] The reaction was carried out in the presence of $H_3PMo_{12}O_{40}$ in place $Cu_{3/2}[PMo_{12}O_{40}]$/SiO_2

[d] The reaction was carried out in the presence of air.

electron- donating and withdrawing groups in the aromatic ring that is 4-methoxy and 4-nitro benzyl alcohols were converted in to their corresponding aldehydes in good isolated yields within 60 and120 minutes. Hetero cyclic alcohols, 2- thiophenemethanol, and 2-pyridinemethanol were oxidized to the corresponding aldehydes in high yields. No oxidation was observed with S and N hetero atoms. Secondary alcohols such as 1-phenyl ethanol required a slightly longer reaction time compared to benzylic alcohol to afford the corresponding Ketone in 65% yields. (Table2 entry 19). In addition a mixture of primary and secondary alcohols was next subjected to oxidation. When benzyl alcohol and 1-phenylethanol were allowed to react, the former oxidized to benzaldehyde in 90% yield and the latter gave acetophenone in <10% yield. This clearly reveals that this method can be applied for the chemo selective oxidation of primary hydroxyl groups in the presence of secondary alcohols. In should be noted that the use of $H_3PMo_{12}O_{40}$ in place $Cu_{3/2}[PMo_{12}O_{40}]$/SiO_2 lead to decrease of the yield in the oxidation reactions (Table 2,entry 21). Oxidation of alcohols using molybdates, leads to one or two electron reduction of molybdenum

Table 3

Comparision of oxidation of benzyl alcohol to benzaldehyde with several catalysts.

Entry	Catalyst	Condition: time (min):yield (%)	Ref.
1	$Cu_{3/2}PW_{12}O_{40}/SiO_2$ [this work]	CH_3CN(reflux) : 70 :90	-
2	$VOSO_4/NaNO_2$	80 °C : 120 : 93	[38]
3	Cu(II) complex- TEMPO	100 °C : 120 : 100	[39]
4	$[Mo_{12}O_{39}(\mu_2\text{-}OH)_{10}H_2\{Co(H_2O)_3\}_4]$	75 °C : 960 : 99	[40]
5	$Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]. 2H_2O$	100 °C : 60 : 99	[23]

from +6 to +5 or +4. Added copper may also reduce from +2 to +1 and facilitate the rapid transfer of electron between anions and the bulk. If air was employed as oxidant instead of pure O_2 the yield of benzaldehyde could reach up to 55% within 2h (Table 2, entry 22).

In order to show the merit of the present work in comparison with recently reported protocols, we compared the results of the dihydropyrimidinones derivative synthesis from various aldehydes in the presence of $Cu_{3/2}PW_{12}O_{40}/SiO_2$, $VOSO_4/NaNO_2$ [38], Cu(II) complex-TEMPO [39], $[Mo_{12}O_{39}(\mu_2\text{-}OH)_{10}H_2\{Co(H_2O)_3\}_4]$ [40] and $Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]. 2H_2O$ [23] with respect to the amounts of the catalysts used, reaction times and yields of the products (Table 3). Comparison of compound $Cu_{3/2}PW_{12}O_{40}/SiO_2$ with these catalysts for this reaction show that activity of $Cu_{3/2}PW_{12}O_{40}/SiO_2$ seems to be higher than or equal with other known catalysts (Table 3).

3.3. Recovery

We investigated the reusability and recycling of $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$. When the reaction was completed, the catalyst was separated by simple filtration and recovered 35 % $Cu_{3/2}[PMo_{12}O_{40}]/SiO_2$ was reused in subsequent reactions without significant decrease in activity even after three runs (Table 4). For 2nd and 3rd runs, filtrates were used for determination of POM leaching. No tungsten and molybdenum were detected in the filtrates by atomic absorption spectroscopy (also proved by XRD, (Fig. 2b)). After third runs, the POMs were leached from the supports (proved by NAA and atomic absorption spectroscopy) and this was led to the deactivation of heterogeneous catalysts. Since in the process of isolation, solvent was used and also because POM was weakly adsorbed on support (adsorption), the catalyst activities of the supported POM decrease after the third time [31].

4. Conclusion

In conclusion, the oxidation of alcohols to aldehydes has been studied with molecular oxygen in the presence of recyclable catalyst 35 % $Cu_{3/2}[PMo_{12}O_{40}]$ /SiO_2 in high yields. This reaction provides a new environmentally friendly route to the conversion of alcoholic function to carbonyl groups. Aldehydes do not undergo further oxidation to carboxylic acids.
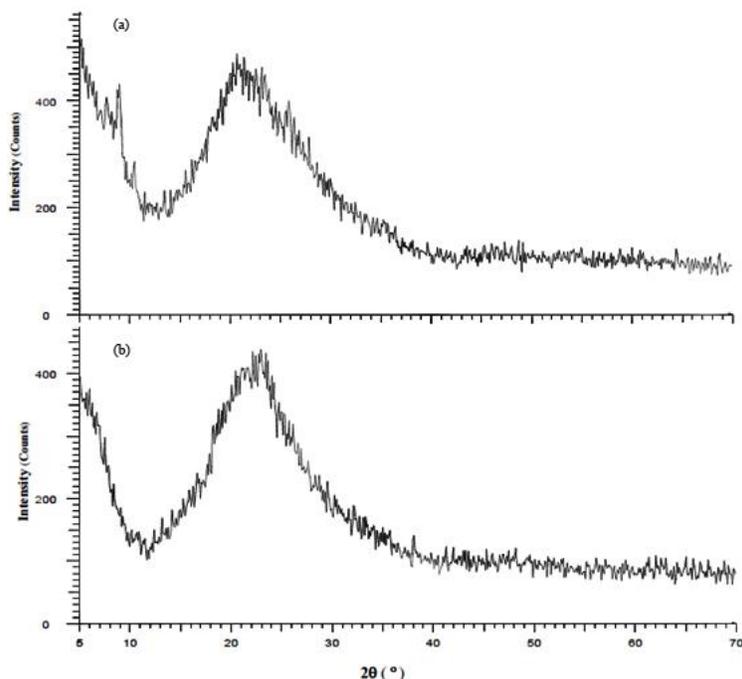
Fig. 2. XRD patternes of (a) 35 % $Cu_{3/2}[PMo_{12}O_{40}]$ /SiO_2 and (b) 35 % $Cu_{3/2}[PMo_{12}O_{40}]$ /SiO_2 after recovery.

Table 4

Recycling of $Cu_{3/2}[PMo_{12}O_{40}]$/SiO_2 in Oxidation of benzyl alcohol.

Run	Yield (%) [a,b,c]
	35% $Cu_{3/2}[PMo_{12}O_{40}]$/SiO_2 (3 mol %)
1	95
2	92
3	92

[a] Isolated yields after column chromatography;

[b] The ^1H NMR approved the reported yields;

[c] The recovered catalyst, washed with CH_2Cl_2, dried and calcined at 400ºC for 3h [31].

Acknowledgments

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