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 aliphatic 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 benzylic alcohol to benzaldehyde (without forming further oxidation products like benzoic acid) is an important organic transformation. This reaction 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 catalytic systems 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$_3$PMo$_{12}$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).

\[
\text{ArCH}_2\text{OH} \xrightarrow{\text{O}_2, \text{CH}_3\text{CN, reflux}} \text{ArCHO} \\
1\text{a-1t} \quad \text{Cu}_{3/2}\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2 \quad 2\text{a-2t}
\]

Scheme 1.

2. Experimental

All materials were commercial reagent grade. H$_3$PMo$_{12}$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. $^1$H 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 $^\circ$C and calcined for 3 h at 400 $^\circ$C (Scheme 2).

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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<sub>2</sub>, pure Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub> and supported Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub> catalysts calcined at 400 °C for 3h. It shows a typical infrared spectrum of silica [35] with bands assigned at 1626 and 821 cm<sup>-1</sup> together with a broad band at 1106 cm<sup>-1</sup> (Fig.1b). The spectrum of pure Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub> shows four bands in the range 1250–500 cm<sup>-1</sup>. These bands are assigned at 1070, 966, 881 and 785 cm<sup>-1</sup>, which are the characteristic bands of the Keggin structure (Fig.1c). These were assigned [36, 37] to ν<sub>as</sub>(P–Oa), ν<sub>as</sub>(Mo–O–Mo), ν<sub>c</sub>(Mo–O–Mo) and ν<sub>as</sub>(Mo–Oc–Mo), respectively. In addition, the observed band at 595 cm<sup>-1</sup> may be attributed to the δ (P–O) vibration [36]. Moreover, the band located at 1619 cm<sup>-1</sup> may be characteristic the O–H stretching vibration. The FT-IR spectrum of Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> indicates that most of characteristic bands of the parent Keggin structure, could be found in HPA fingerprint region (1250–500 cm<sup>-1</sup>), are not shown or appeared in the same assignable position of the bands correspond to SiO<sub>2</sub> host material (Fig.1a). Fig. 2a shows the XRD patterns of 35 % Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> within the 20 range of 5–70°. The peaks corresponding to amorphous 35 % Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> are present. No peaks from any crystalline form of Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub> could be observed, indicating that Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub> was inserted into SiO<sub>2</sub> matrix.

3.2. Oxidation of Benzylic Alcohols Catalyzed by Cu<sub>3/2</sub>[PMo<sub>12</sub>O<sub>40</sub>]/SiO<sub>2</sub>

The influence of the various solvent on the yield of the reaction was investigated using of benzy 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 benzy alcohol was examined as a standard substrate in the presence of a 0.4g catalyst in CH<sub>3</sub>CN under O<sub>2</sub> 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
The reaction was carried out in the presence of H$_2$PMO$_{12}$O$_{40}$/SiO$_2$, VOSO$_4$/NaNO$_2$ [38], Cu(II) complex-TEMPO [39], [Mo$_2$O$_{7}$OH$_2$(H$_2$O)$_2$]$_{4}^{2-}$ [40] and Na$_{6}$Fe$_{3}$[AlMO$_{12}$O$_{40}$]$_{2}$H$_2$O [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 leach 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 patterns 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

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<tr>
<th>Run</th>
<th>Yield (%) $^{abc}$</th>
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<tr>
<td></td>
<td>35% Cu$<em>{3/2}$[PMo$</em>{12}$O$_{40}$]/SiO$_2$ (3 mol %)</td>
</tr>
<tr>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
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<td>3</td>
<td>92</td>
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$^a$ Isolated yields after column chromatography;
$^b$ The $^1$H NMR approved the reported yields;
$^c$ The recovered catalyst, washed with CH$_2$Cl$_2$, dried and calcined at 400°C for 3h [31].

Acknowledgments

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References