

## Heteropolyoxometalate Catalyzed Selective Oxidation of Alcohols to Carbonyl Compounds by Hydrogen Peroxide under Mild Condition

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### Abstract

Keggin-type heteropolyoxometalates have been used as catalysts for the oxidation of benzylic alcohols and secondary alcohols to the corresponding carbonyl compounds using environment-friendly  $\text{H}_2\text{O}_2$  as oxidant at room temperature. The catalysts used in this study exhibit high selectivity in the oxidation of alcohols with no over-oxidation and formation of carboxylic acids. For vanadium(V)-substituted heteropolyoxometalates  $[\text{H}_{x-2}\text{PV}_x\text{W}_{12-x}\text{O}_{40}]^{5-}$  ( $x = 4$  and  $6$ ), the catalytic activity decreased with the increase in number of vanadium atoms in the catalyst.

**Key Words:** Heteropolyoxometalate; Oxidation; Alcohols; Hydrogen peroxide

### Introduction

Selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most important functional group transformations in organic synthesis (Sheldon et al., 1981). The carbonyl compounds represent an important class of products and intermediates in the fine chemicals (Köckritz et al., 2006). Thus, several methods have been explored to accomplish selective oxidation of alcohols to more valuable carbonyl compounds (Sheldon et al., 2000). Traditional methods used for this purpose generally involve inorganic oxidants (Holum et al., 1961) such as PCC,  $\text{MnO}_2$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{NaOCl}$  and  $\text{KMnO}_4$ . However, most of these oxidants are toxic, hazardous, or required in large excess. Sometimes a large amount of toxic waste is also generated. Therefore, the development of catalytic oxidation process for selective oxidation of alcohols using safer, inexpensive and environmentally benign oxidizing agents such as molecular oxygen and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) remains a critical challenge. Many highly efficient systems have been developed for catalytic alcohol oxidation with molecular oxygen using Pd (Brink et al., 2000), Ru

(Matsushita et al., 1999), Cu (Semmelhack et al., 1984), Co (Iwahama et al., 1995), Pt (Jia et al., 1994), Os (Shapley et al., 2000), Ni (Choudary et al., 2001) and polyoxometalates catalysts (Khenkin et al., 2001). But since aerobic oxidation is often difficult to control, it makes the use of molecular oxygen challenging.  $\text{H}_2\text{O}_2$  due to its clean and environmental friendly nature. Besides water as the sole by-product, it provides a high content of active oxygen species and is much cheaper and safer than organic peroxides or peracids (Anastas et al., 2000). Consequently, the catalytic oxidation of alcohols using  $\text{H}_2\text{O}_2$  has received much attention from the viewpoint of green chemistry.

Polyoxometalates (POMs) have been attracting considerable interest over recent years as oxidation catalysts due to their multifunctionality and structural mobility (Pope, 1983). The activities of the polyoxometalates can be controlled by both changing the heteroatom and the oxometalate moiety, thus making them suitable for particular research. Keggin-type heteropolyoxometalates have many advantages that make them economical and environmentally attractive in both academic and industrial

applications; they are useful as acid and oxidation catalysts for various reactions since their catalytic features can be varied at a molecular level (Okuhara and Misono, 1996). Recently, the catalytic oxidation of alcohols using  $\text{H}_2\text{O}_2$  has received much attention from the viewpoint of green chemistry. Most examples of alcohol oxidation using polyoxometalates (POM) as catalysts and  $\text{H}_2\text{O}_2$  as an oxidant (Ishii et al., 1988) were presented.

Herein, we present an environment-friendly and efficient oxidation of alcohols catalyzed by heteropolyoxometalate  $[\text{H}_{x-2}\text{PV}_x\text{W}_{12-x}\text{O}_{40}]^{5-}$  ( $x = 4$  and  $6$ ) with  $\text{H}_2\text{O}_2$  as oxidant under mild reaction conditions. The synthesized heteropolyoxometalates selectively oxidize alcohols to their corresponding carbonyls with high yield. The effect of different reaction parameters on the catalytic activity of vanadium substituted polyoxometalates has also been examined in this study.

## Materials and Methods

All chemicals used for the synthesis were purchased from Sigma Aldrich, Bangalore, India and were used without further purification. Alcohol substrates were purchased from Sigma Aldrich and used as received. All the solvents used for the catalytic experiments were distilled under argon prior to use. The active oxygen content of the oxidant  $\text{H}_2\text{O}_2$  (as ~30% solution in water) was determined iodometrically prior to use. The product analyses were done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column). The identification and quantification of the products were done from the response factors of standard compounds.

## Experimental Procedures

### Syntheses of Catalysts

#### Potassium Salt of the Heteropolyoxometalates

Potassium salts of the heteropolyoxometalates,  $\text{K}_5[\text{H}_{x-2}\text{PV}_x\text{W}_{12-x}\text{O}_{40}]$  ( $x = 4$  and  $6$ ) were synthesized and characterized according to the published method (Smith and Pope, 1973).

#### Tetra-n-butylammonium (TBA) Salt of the Heteropolyoxometalates

The potassium salt of  $[\text{H}_{x-2}\text{PV}_x\text{W}_{12-x}\text{O}_{40}]^{5-}$  ( $x = 4$  or  $6$ ) was dissolved in 3 M HCl and the pH of the solution was adjusted to 2.0. The mixture was gently stirred for 5 min. The solution was filtered off and tetra-n-butylammonium bromide, TBABr (slightly greater than 5 times of potassium salts) was added with vigorous stirring. The resulting orange yellow precipitate was collected by filtration and then washed with an excess amount of water and dried in vacuo. Recrystallization from acetonitrile gave analytically pure tetra-n-butylammonium (TBA) salt of the polyoxometalates.

#### $[(\text{C}_4\text{H}_9)_4\text{N}]_5[\text{H}_2\text{PV}_4\text{W}_8\text{O}_{40}]$ , POM 1

Yield: 68%. Analytically Calculated for  $[(\text{C}_4\text{H}_9)_4\text{N}]_5[\text{H}_2\text{PV}_4\text{W}_8\text{O}_{40}] \cdot \text{H}_2\text{O}$ : C, 26.9; H, 5.18; N, 1.96; P, 0.87; V, 5.7; W, 41.1; Found C, 27.1; H, 5.14; N, 1.88; P, 0.85; V, 5.85; W, 40.8%.

#### $[(\text{C}_4\text{H}_9)_4\text{N}]_5[\text{H}_4\text{PV}_6\text{W}_6\text{O}_{40}]$ , POM 2

Yield: 64%. Analytically Calculated for  $[(\text{C}_4\text{H}_9)_4\text{N}]_5[\text{H}_4\text{PV}_6\text{W}_6\text{O}_{40}] \cdot \text{H}_2\text{O}$ : C, 29.0; H, 5.66; N, 2.1; P, 0.93; V, 9.2; W, 33.3; Found C, 29.2; H, 5.54; N, 2.15; P, 0.91; V, 9.14; W, 33.1%.

## General Procedure for Alcohol Oxidation

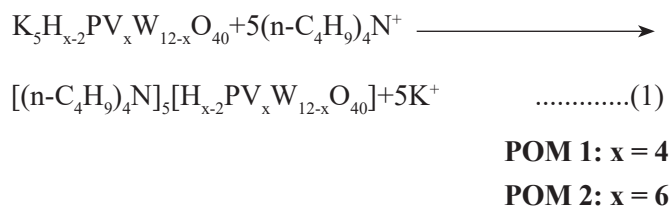
Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical experiment, the alcohol substrate and the catalyst was dissolved in a mixture of acetonitrile and dichloromethane (1:1, v/v). The oxidation reaction was initiated by adding 2 mM of  $\text{H}_2\text{O}_2$  and the contents were stirred at room temperature by using magnetic bar. The progress of the reaction was monitored by GC. After completion of the reaction, the reaction mixture was directly injected into a capillary column of a preheated GC after adding a standard solution of pentafluoriodobenzene (PFIB) as an internal standard. To establish the identity of the alcohols and carbonyl compounds unequivocally, the retention times and spectral data were compared to those commercially available compounds. The quantization of the products was done from the response factors of standard product samples as usual.

## Results and Discussion

### Preparation and Characterisation of the Catalysts

The potassium salt of the heteropolyoxometalates  $[H_{x-2}PV_xW_{12-x}O_{40}]^{5-}$  ( $x = 4$  and  $6$ ) were prepared following the known procedure (Smith and Pope, 1973).

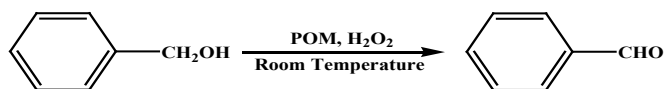
The heteropolyoxometalates in the form of potassium salt,  $K_5[H_{x-2}PV_xW_{12-x}O_{40}]$  ( $x = 4$  and  $6$ ), are dissolved well in water, but are insoluble in organic solvents in which the catalytic experiments were carried out. Hence, an attempt was made to synthesize the catalysts as the alkyl ammonium salts in order to improve their solubility in common organic solvents. This has been achieved successfully by exchanging the potassium ions of the heteropolyoxometalates with tetra-*n*-butylammonium (TBA) ions by adding tetra-*n*-butylammonium bromide (TBABr) to the solution of potassium salts of the heteropolyoxometalates in 3 M HCl under stirring condition at room temperature (equation 1).



The desired catalysts were precipitated immediately because of the poor solubility in water. The crude product was then recrystallized from acetonitrile as orange yellow powder. The synthesized catalysts in the form of TBA salts are characterized by elemental analysis. The data from elemental analysis matched well with the proposed molecular formula.

### Oxidation of Alcohols

The TBA salts of heteropolyoxometalates have been explored as catalysts for the oxidation of alcohols at room temperature with  $H_2O_2$  as terminal oxidant. The oxidation of benzyl alcohol was chosen as the model reaction (Scheme 1).



**Scheme 1** Catalytic oxidation of benzyl alcohol with  $H_2O_2$  at room temperature.

The effect of different reaction parameters such as nature of the solvent, substrate/catalyst concentration have been studied to optimize the reaction conditions in order to achieve maximum yield of alcohol oxidation reactions.

### Effect of Solvent

The solvent plays an important role in the catalytic oxidation of alcohols in the presence of  $H_2O_2$  as oxidant. The influence of nature of the solvent on the oxidation of benzyl alcohol was studied using three different solvents viz. dichloromethane ( $CH_2Cl_2$ ), acetonitrile ( $CH_3CN$ ), and mixture of acetonitrile ( $CH_3CN$ ) and dichloromethane ( $CH_2Cl_2$ ) (1:1, v/v) at room temperature with **POM1** as catalyst. The results are summarized in Table 1. The other parameters such as concentration of substrate, catalyst and  $H_2O_2$  were kept constant in each solvent system.

**Table 1** Oxidation of benzyl alcohol catalyzed by **POM 1** in different solvents<sup>a</sup>

Entry	Solvent	Yield (%) <sup>b</sup>
1	$CH_2Cl_2$	34
2	$CH_3CN$	58
3	$CH_3CN/CH_2Cl_2$ (1:1, v/v)	83

<sup>a</sup>Reaction conditions: Benzyl alcohol (100 mM), **POM 1** (50  $\mu$ M),  $H_2O_2$  (2 mM) in 2 mL solvent, 12 h. <sup>b</sup>Yields are based on the concentration of the oxidant.

The results revealed that oxidation of benzyl alcohol strongly depends on the nature of the solvent. Among the solvent used, a mixed solvent of acetonitrile and dichloromethane (1:1, v/v) gave the highest yield of benzaldehyde and the order of efficiency of the catalyst in terms of yield follows the order  $CH_2Cl_2 < CH_3CN < CH_3CN/CH_2Cl_2$  (1:1, v/v).

### Optimization of Substrate/Catalyst Concentration

After selecting the best solvent system for the oxidation of benzyl alcohol catalyzed by **POM1** with  $H_2O_2$ , the influence of concentration of substrate with fixed concentration of catalyst (50  $\mu$ M) and  $H_2O_2$  (2 mM) (Table 2, entries 1-4) as well as the effect of concentration of catalyst

keeping substrate (100 mM) and  $\text{H}_2\text{O}_2$  (2 mM) concentration fixed (Table 2, entries 3, 5 and 6) has been studied. The results are compiled in Table 2.

**Table 2** Optimization of substrate/catalyst concentration<sup>a</sup>

Concentration of				
Entry	Substrate (mM)	Catalyst ( $\mu\text{M}$ )	$\text{H}_2\text{O}_2$ (mM)	Yield (%) <sup>b</sup>
1	20	50	2	24
2	50	50	2	46
3	100	50	2	83
4	200	50	2	82
5	100	25	2	52
6	100	100	2	82
7	100	0	2	6
8	100	50	0	2

<sup>a</sup>Reaction conditions: Substrate: benzyl alcohol, catalyst: **POM 1**, oxidant:  $\text{H}_2\text{O}_2$ , solvent: 2 mL mixture of  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (1:1, v/v), 12 h. <sup>b</sup>Yields are based on the concentration of the oxidant.

These results suggest that with fixed concentration of catalyst (50  $\mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  (2 mM), the best yield of benzaldehyde was obtained using 100 mM concentration of benzyl alcohol (entry 3). On the other hand, the reactions without catalyst or oxidant, as shown in entry 7 and 8, obtain only 6% and 2% yields of benzaldehyde respectively. As the results, the POM catalysts play an important role in the oxidation reaction.

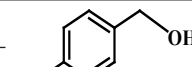
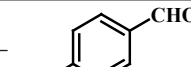
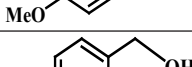
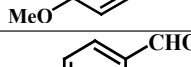
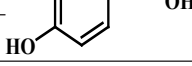
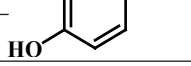
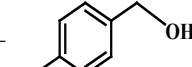
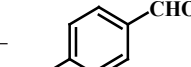
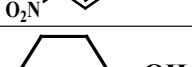
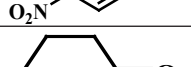
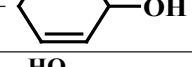
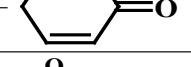

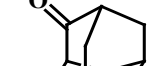
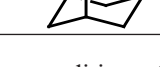
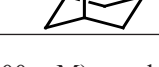
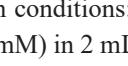
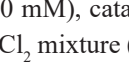
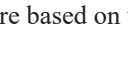
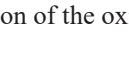
After optimizing the reaction conditions using **POM1** as catalyst, oxidation of benzyl alcohol was next studied with **POM2** as catalyst. Here, 64% conversion of benzaldehyde was observed under optimized reaction conditions. The oxidation of benzyl alcohol with both the catalysts suggested that **POM2** catalyst was less effective. This suggested that number of vanadium atoms in the heteropolyoxometalate catalyst plays a key role for the alcohol oxidation by  $\text{H}_2\text{O}_2$ .

## Oxidation of a Series of Alcohols

To study the scope for this procedure, the oxidation of a variety of alcohols has been studied under the optimized reaction conditions. Oxidation of a variety of benzyl alcohol derivatives and secondary alcohols were carried out and the results are presented in Table 3. Substituted benzyl alcohols having electron-withdrawing and -donating group in the aromatic ring were converted into corresponding benzaldehyde derivatives at room temperature with very good yields (Table 3, entries 1-6). Quantitative conversion of 4-methoxybenzyl alcohol and 4-hydroxybenzyl alcohol has been achieved based on the initial concentration of  $\text{H}_2\text{O}_2$  by **POM1** as catalyst (Table 3, entries 1, 3).

The presence of an electron-withdrawing or -donating group in the aromatic ring has no significant effect on the reaction yield, but decreases the reaction time appreciably. It is worth mentioning that no oxidation was observed in the aromatic ring of the benzylic substrates. Secondary alcohols (2-cyclohexen-1-ol and 2-hydroxy adamantane) have also been converted to corresponding ketone with moderate to high yields (Table 3, entries 7-10). As the results, no over-oxidation by-product (i.e. carboxylic acid) has been detected even after extended reaction times.

**Table 3** Oxidation of alcohols by  $\text{H}_2\text{O}_2$  catalyzed by heteropolyoxometalates at room temperature<sup>a</sup>

Entry	Substrate	Catalyst	Product	Yield (%) <sup>b</sup>
1		POM 1		100
2		POM 2		85
3		POM 1		100
4		POM 2		88
5		POM 1		90
6		POM 2		89
7		POM 1		85
8		POM 2		74
9		POM 1		54
10		POM 2		42

<sup>a</sup>Reaction conditions: Substrate (100 mM), catalyst (50  $\mu\text{M}$ ),  $\text{H}_2\text{O}_2$  (2 mM) in 2 mL  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  mixture (1:1, v/v), 8 h.

<sup>b</sup>Yields are based on the concentration of the oxidant.

### Comparison of Efficiency of the Catalysts

The efficiency of both heteropolyoxometalate catalysts has also been examined. It has been found that number of vanadium atoms in the POM catalysts play an important role in alcohol oxidation by  $H_2O_2$ . It is clear from Table 3 that the catalytic efficiency towards alcohol oxidation decreases with the increase in number of vanadium atoms in the catalyst (Kanjina and Trakarnpruk, 2009). The lower number of vanadium, **POM 1**, represents the better catalyst in oxidizing alcohols to corresponding carbonyl compounds.

### Conclusion

The synthesized heteropolyoxometalates **POM1** and **POM2** selectively oxidized benzylic alcohols and secondary alcohols to the corresponding carbonyl compounds in high yields at room temperature using environmentally benign  $H_2O_2$  as an oxidant without the formation of any over-oxidation products. Using benzyl alcohol as substrate, reaction conditions have been optimized considering different parameters to achieve maximum yield of alcohol oxidation reactions. This reaction provides an environmentally friendly route to the conversion of alcoholic functions to the carbonyl groups.

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