Short Communication

Heteropolyoxometalate Catalysts for Oxidation of Alcohols with H_2O_2 Under Green Condition

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Abstract

This work describes the use of hydrogen peroxide as an oxidant for the selective oxidation of cyclohexanol and benzyl alcohol under green condition using heteropolyoxometalates catalysts. The results showed that catalytic activity depended on types of countercation and metal of the catalysts. For transition metal-substituted polyoxotungstates $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}M(H_2O)O_{39}]$, the catalytic order is Ni > Co > Mn. For a series of vanadium(V)-substituted polyoxotungstates $[(n\text{-}C_4H_9)_4N)]_{3+x}[PW_{12-x}V_xO_{40}]$, the catalytic activity decreased with increasing numbers of vanadium atoms in the catalyst. Using the $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$ as a catalyst, cyclohexanol was oxidized to cyclohexanone with 98% yield and 100% selectivity at 90°C in 5 h whereas benzyl alcohol was oxidized to benzaldehyde with 96% yield and 37% selectivity to benzaldehyde and 63% selectivity to benzoic acid at 90°C in 12 h.

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

Introduction

The oxidation of alcohols to aldehydes or ketones is a vital reaction in synthetic organic chemistry. Oxidation using homogeneous catalysts (Sheldon et al., 2000), supported metal ions and heterogeneous catalysts have been reported (Yang et al.,2000; Maldotti et al.,2002). From the environmental point of view, oxidation reactions with green oxidant like H_2O_2 are desirable as its by-product is water. Polyoxometalates are unique catalytic materials, due to their multifunctionality and structural mobility. Their activities can be controlled by changes in the metal center and the counter cation (Trost et al., 1984; Wang et al., 2005). Metal-substituted heteropolyoxometalates have many similarities to metal complexes of macrocyclic ligands, metalloporphyrins and related species, because they posses rigid co-ordination sites surrounding a metal centre (Hill et al., 1994). Heteropolyoxometalates catalyzed oxidation reactions have been studied (Weng et al., 2007; Komintarachat et al., 2006; Kozhevnikov et al., 1995; Lingaiah et al., 2006; Peng et al., 2001). Oxidations with hydrogen peroxide using polyoxometalates, for example, $[Na_6SiW_{11}ZnH_2O_{40}]12.H_2O$ (Wang et al., 2005), $C_{16}H_{33}N(CH_3)_3]_3PW_4O_{16}$ (Zhang et al., 2007), $[n\text{-}C_7H_7N(CH_3)_3]_7PW_{11}O_{39}$ (Weng et al., 2008), and $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$ (Zhang et al., 2008) have been reported (Ishii et al., 1988; Neumann et al.,1995; Venturello et al., 1991). Polyoxometalates were also used as a supported catalyst (Manyar et al., 2006).

In this work, an oxidation of cyclohexanol and benzyl alcohol catalyzed by different types of polyoxometalates using a clean oxidant, H_2O_2 and under solvent-free condition was reported. The reusability and stability of the catalysts were also investigated.

Experimental Procedures

Syntheses of Catalysts

$H_3[PMo_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $Na_2H[PMo_{12}O_{40}]$, $Na_2H[PW_{12}O_{40}]$ (Silviani et al., 2004); $[(n\text{-}C_4H_9)_4N)]_3[PMo_{12}O_{40}]$, $[(n\text{-}C_4H_9)_4N)]_3[PW_{12}O_{40}]$ (Deltcheff et al., 1983); vanadium(V)-substituted polyoxotungstates $[(n\text{-}C_4H_9)_4N)]_{3+x}$ $[PW_{12-x}V_xO_{40}]$, (x = 0-3) (Himeno et al., 1998); and $[(n\text{-}C_4H_9)_4N]_4H$ $[PW_{11}M(H_2O)O_{39}]$ (M = Mn, Co or Ni) (SimÕes et al. 1999) were synthesized and characterized according to the literatures.

Oxidation Reaction

In a 100 ml flask equipped with a reflux condenser and a magnetic stirrer, a catalyst (10 μmol) and an alcohol (6.7 mmol) were added. Then H_2O_2 (13.5 mmol) was slowly added and the reaction mixture was stirred at different temperature and time. The mixture was then cooled to room temperature. The catalyst was separated by centrifuging. Liquid phase was added with 2 mL of 25% H_2SO_4 and the reaction products were extracted with diethyl ether. The organic layer was neutralized with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. Product yield was determined by GC (a Varian CP-3800, equipped with a CP-Wax column (30 m. x 0.32 mm.) and FID as detector). After the reaction, the catalyst was separated, washed with hexane, dried and reused.

Results and Discussion

The oxidation of cyclohexanol was performed to compare activity of different heteropolyoxometalates under the same reaction condition: 10 μmol catalyst, 6.7 mmol cyclohexanol, 13.4 mmol H_2O_2, at 90°C and 5 h reaction time. The results are shown in Table 1. Reaction controls were carried out in the absence of catalyst and in the absence of oxidant (separately). Only 6% and 0% yields of cyclohexanone were obtained, respectively. The catalysts in the proton and sodium forms were dissolved well in water, the oxidation reaction occurred in biphasic (alcohol-water) system. On the contrary, the catalysts possessing tetrabutylammonium cation were neither dissolved in water nor the substrate alcohol. Even after addition of H_2O_2, the catalyst was still not dissolved. Therefore, in this work the reaction was heterogeneous. It was reported (Zhang et al., 2008) that the heteropolyoxometalate catalyst was found to be dissolved during the oxidation reaction in acetonitrile but it precipitated from the reaction at the end of the reaction. This might demonstrate that the active species produced during the reaction can be dissolved in acetonitrile. In this work when temperature was raised to 100°C, yield was decreased due to more rapid decomposition of H_2O_2.

The catalytic activity of the catalysts depended on a type of countercation: quaternary ammonium > sodium > proton. The increase in activity of the $H_3[PW_{12}O_{40}]$ catalyst when proton was substituted with sodium was previously reported for oxidation of benzyl alcohol (Yadav et al., 2001). The identity of the addenda atoms (Mo or W) had an effect on catalytic activity. The heteropolyoxotungstates show higher activity than the heteropolyoxomolybdates due to higher acidity of the former catalysts. For a series of vanadium (V) - substituted polyoxotungstates $[(n\text{-}C_4H_9)_4N)]_{3+x}[PW_{12-x}V_xO_{40}]$ and transition metal substituted-polyoxotungstates, $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}M(H_2O)O_{39}]$, the catalytic activity orders are $V_1 > V_2 > V_3$ and Ni > Co > Mn, respectively. This trend indicates that the activity is governed by the reduction potential of the catalyst (Song et al., 2004). The similar trend of catalytic activity was reported for aerobic oxidation of aldehyde (Silviani et al., 2004). It should be mentioned that, in this work, a phase transfer agent was not required since the quaternaryammonium polyoxometalates are lipophilic.

Table 1 Oxidation of cyclohexanol by hydrogen peroxide.

Catalyst	%Yield of cyclohexanone
$H_3[PMo_{12}O_{40}]$	20
$H_3[PW_{12}O_{40}]$	44
$Na_2H[PMo_{12}O_{40}]$	25
$Na_2H[PW_{12}O_{40}]$	50
$[(n\text{-}C_4H_9)_4N]_3[PMo_{12}O_{40}]$	27
$[(n\text{-}C_4H9)_4N]_3[PW_{12}O_{40}]$	82
$[(n\text{-}C_4H_9)_4N]_4[PW_{11}VO_{40}]$	93
$[(n\text{-}C_4H_9)_4N]_5[PW_{10}V_2O_{40}]$	59
$[(n\text{-}C_4H_9)_4N]_6[PW_9V_3O_{40}]$	60
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$	90
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$	98
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Mn(H_2O)O_{39}]$	88

Reaction conditions: 6.7 mmol cyclohexanol, 10 µmol catalyst, 13.4 mmol H_2O_2, 90°C, 5 h.

All catalysts oxidized cyclohexanol to cyclohexanone with 100% selectivity.

The oxidation of benzyl alcohol was also performed under the same reaction conditions as used in the oxidation of cyclohexanol using $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$, $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$ and $[(n\text{-}C_4H_9)_4N]4H[PW_{11}Mn(H_2O)O_{39}]$ as a catalysts. The results are shown in Table 2. The activity order was found to be in the same trend as that for cyclohexanol oxidation.

Table 2 Oxidation of benzyl alcohol by hydrogen peroxide.

Catalyst	% Total yield of benzaldehyde and benzoic acid
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$	52
$[(n\text{-}C4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$	59
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Mn(H_2O)O_{39}]$	49

Reaction conditions: 6.7 mmol benzyl alcohol, 10 µmol catalyst, 13.4 mmol H_2O_2, 90°C, 5 h.

The $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$ which showed the best performance was chosen for the study of reaction as a function of time. As shown in Figure 1, at 4 h, 52% yield with 75% selectivity to benzaldehyde and 25% selectivity to benzoic acid were obtained. It can be seen that % yield increased with time. After 12 h, 96% yield can be obtained but the selectivity to benzaldehyde was dropped (37%) while the selectivity to benzoic acid was increased (63%). This result indicated that the initial product, benzaldehyde, was further oxidized to benzoic acid.

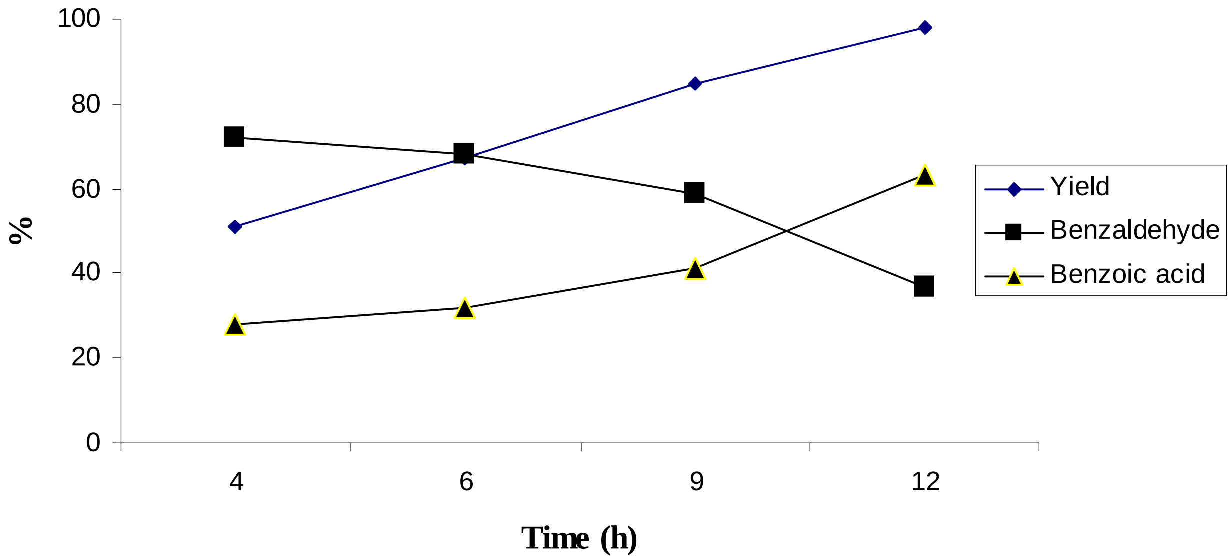

Figure 1 Yield and selectivity from catalytic oxidation of benzyl alcohol as a function of reaction time. Reaction conditions: benzyl alcohol 6.7 mmol, $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$ catalyst 10 µmol, H_2O_2 13.4 mmol and 90°C.

The reusability of catalyst was investigated. The catalysts was filtered, washed with hexane and subjected to subsequent runs of cyclohexanol oxidation with the fresh substrate. The catalytic activities after three runs were almost unchanged in yields (98 %, 97% and 96%). This indicated that the catalyst was stable.

Conclusions

Heteropolyoxometalates are efficient catalyst for selective oxidation of cyclohexanol and benzyl alcohol using environmental friendly oxidant in the absence of organic solvent or phase transfer agent. They can be easily recycled.

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