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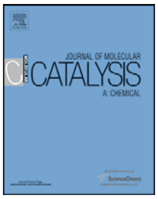

Secondary alcohols oxidation with hydrogen peroxide catalyzed by $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$: Transform-and-retransform process between catalytic precursor and catalytic activity species

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ABSTRACT

$[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$ (**1a**) catalyzed the oxidation of secondary alcohols with 27.5% aqueous hydrogen peroxide under solvent-free conditions. The isolated yields of all ketones were higher than 92%. The turnover number of the catalyst **1a** was above 368, and the highest TON and TOF were up to 3840 and 320 h^{-1}. In this catalytic system, the catalytic active species was $\{PO_4[WO(O_2)_2]_4\}^{3-}$, which was formed from **1a** in the reaction. It was discovered that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (PW_4) and $[PW_{12}O_{40}]^{3-}$ (PW_{12}) kept an equilibrium during the alcohol oxidation by simultaneous monitoring the distribution of species in organic and aqueous phases. The analysis of the W content in the aqueous phase by ICP and the detection of the species transformation in the organic phase by ^{31}P NMR revealed that the most of the PW_4 species were transformed to the PW_{12} species again after the reaction. PW_{12} and PW_4 were in the transform-and-retransform process.

1. Introduction

The oxidation of alcohols into the corresponding carbonyl compounds is one of the most vital functional group transformations in organic synthesis [1]. Many traditional inorganic oxidants for alcohols oxidation are well known [2], such as PCC, MnO_2, $Na_2Cr_2O_7$, NaClO, $KMnO_4$; however, usually these reagents are hazardous or toxic. Due to the economic and environmental viewpoints, the quest for developing the clean and atom economy [3] catalytic oxidation process for converting alcohols to carbonyl compounds on an industrial scale which employs safer and inexpensive oxidants, such as molecular oxygen or hydrogen peroxide, remains an important challenge.

Molecular oxygen is obviously the cheapest and ideal oxidant. A great deal of results [4] was reported on alcohol oxidation with oxygen as an oxidant, such as Sheldon's PhenS-Pd$(OAc)_2$ and $CuBr_2$/TEMPO/Bipy/t-BuOK, Ragauskas's acetamido-TEMPO/$Cu(ClO_4)_2$/TMDP/DABCO and $VO(acac)_2$/DABCO-[BMIM]PF_6, Neumann's $H_5[PV_2Mo_{10}O_{40}]$, Ishii's NHPI/$Co(Ac)_2$, Hu's $NaNO_2/Br_2$/TEMPO and Wang's Pd/Al_2O_3 and so on. Excellent yields of carbonyl compounds were obtained in these systems under mild conditions. Hydrogen peroxide is also a very attractive and clean oxidant for liquid-phase oxidation. Besides water as the sole byproduct, it provides a high content of active oxygen species and is much cheaper and safer than organic peroxides or peracids [5]. Recently, the catalytic oxidation of alcohols using hydrogen peroxide has received much attention from the viewpoint of green chemistry. Most examples of alcohol oxidation employed polyoxometalates (POM) [6] as catalysts and hydrogen peroxide as an oxidant. For example, $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$, $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$, $[n\text{-}(C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$, $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3[PW_4O_{16}]$, $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, $[BMIM]_3\{PO_4[WO(O_2)_2]_4\}$-[BMIM]$PF_6$, $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$, $Na_6[SiW_{11}ZnH_2O_{40}]\cdot 12H_2O$ and $[NaP_5W_{30}O_{110}]^{14-}$ were shown to catalyze the oxidation of alcohol with hydrogen peroxide as a primary oxidant.

During the POM catalytic oxidation, mostly active oxygen species were firstly formed from H_2O_2 by reacting with the catalyst and then oxidized alcohols. The 12-phosphotungstate catalyst with the Keggin structure is a kind of Venturello–Ishii catalyst

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which was successfully applied to the catalytic alkene epoxidation [6a,7]. It was proved that PW_{12} was first degraded to PW_4 by excess hydrogen peroxide, and that PW_4 was the active species in the Venturello–Ishii catalytic system [8]. Meanwhile, PW_{12} could also be applied to the catalytic alcohols oxidation [6a]. Ikegami and co workers developed a new recyclable catalytic system comprising 12-phosphotungstic acid and a temperature-responsive polymer support and used it for the catalytic alcohol oxidation; the recovered catalyst was unchanged and no other species were evident [9]. The fact that PW_{12} just formed PW_4 in the hydrogen peroxide oxidation reaction was reported in literature [8], but they did not mention that PW_4 could be transformed to PW_{12}, and did not expatiate on the transforming relationship between PW_4 and PW_{12}, especially in alcohol oxidation.

Here we present an environment-friendly and efficient procedure for the secondary alcohol oxidation catalyzed by $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$ using 27.5% aqueous hydrogen peroxide under solvent-free conditions. Ketone was produced satisfactorily from secondary alcohol oxidation with high TON and TOF. In this catalytic system, ^{31}P NMR spectra and ICP data showed that PW_{12} was partially degraded to PW_4 by its reaction with H_2O_2, and the residual PW_{12} and PW_4 were in equilibrium during the oxidation process. Meanwhile, it was found that PW_4 was transformed to PW_{12} again after the reaction. The novel transform-and-retransform process was first discovered between PW_{12} and PW_4 in the alcohol oxidation, which was different from the oxidation process using PW_{12} as a catalyst reported previously. The transforming relationship between PW_4 and PW_{12} was elaborated in this work.

2. Experimental

2.1. General

GC analysis was performed by an Agilent 6820 gas chromatograph with an FID detector equipped with a 2 m × 2 mm id.10%QF-1 80–100 mesh Chromosorb WHP stainless steel packed column. The ^{31}P NMR spectra were recorded at 9.4 T by a Bruker DRX 400 spectrometer. The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz by BBO MAS probe head using 4 mm ZrO_2 rotors, 2.0 μs pulse, 2 s repetition time and 2048 scans, with samples spun at 8 kHz and referenced to 85% H_3PO_4. The ^{31}P NMR spectra of the catalysts in solvents were obtained by a BBI 5 mm converse phase broadband probe head using real sample solution with D_2O internal tube locking field. The IR spectra were carried out on a Bruker TENSOR 27 FTIR spectrometer in a transmission mode (32 scans, 1 cm^{-1} resolution) with a KBr pellet, and OPUS software (Version 4.0) was used for spectra acquisition and processing. Commercially available organic and inorganic compounds were used without further purification.

2.2. Preparation of catalysts ***1a***–***8a***

A solution of 12-phosphotungstic acid (4.32 g, 1.5 mmol) in distilled water (20 ml) was added dropwise to a solution of corresponding alkyl ammonium chloride (4.5 mmol) in distilled water (80 ml) while stirring vigorously (Eq. (1)). The solution of 1:1(v/v) acetone and distilled water was used to dissolve the alkyl ammonium chloride during the preparation of **6a**, **7a** and **8a**. The white precipitate of alkylammonium 12-phosphotungstate appeared immediately, and then the suspended solution continued to be stirred for 1 h. The white precipitate was filtered, washed with distilled water twice, and dried 24 h under low pressure.

$$\underset{\mathbf{a}}{H_3PW_{12}O_{40}} + 3Q^+ \longrightarrow \underset{\mathbf{1a}}{Q_3PW_{12}O_{40}} + 3H^+$$

$$\begin{aligned}
&Q^1{=}n\text{-}C_{16}H_{33}N^+(CH_3)_3\\
&Q^2{=}(CH_3)_4N^+\\
&Q^3{=}(n\text{-}C_4H_9)_4N^+\\
&Q^4{=}n\text{-}C_{12}H_{25}N^+(CH_3)_3\\
&Q^5{=}(n\text{-}C_{12}H_{25})(C_7H_7)N^+(CH_3)_2\\
&Q^6{=}(n\text{-}C_{18}H_{37})(C_7H_7)N^+(CH_3)_2\\
&Q^7{=}(n\text{-}C_{18}H_{37})_2N^+(CH_3)_2\\
&Q^8{=}(n\text{-}C_8H_{17})_3N^+CH_3
\end{aligned} \qquad (1)$$

2.3. General procedure for oxidation of alcohols

Reactions were carried out in a 70 ml closed pressure glass tube equipped with magnetic stirring at 363 ± 0.5 K for about 6–12 h. The alcohol, hydrogen peroxide (27.5%) and catalyst were in a corresponding ratio. The reaction solution was sampled and analyzed by GC using an internal standard technique, and the yield was based on hydrogen peroxide. In the large-scale (500 mmol) reaction, the reaction was carried out in a three-neck round-bottom flask and hydrogen peroxide was added dropwise to the alcohol under refluxing. The products were identified by comparison of their mass and NMR spectra with those of authentic samples. The catalyst was precipitated and recovered by adding diethyl ether into the reactor after the reaction. After the precipitation was completed, the recovered **1a** was separated by centrifugation and reused after washed by diethyl ether and dried under air.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

A series of catalysts (**1a**–**8a**) was synthesized by mixing 12-phosphotungstic acid with three equivalents of various ammonium cations in water at room temperature for 1 h. All the desired catalysts were precipitated immediately after mixing phosphotungstic acid and ammonium cations because of the poor solubility in water. Then the insoluble catalysts were washed with distilled water and dried in a vacuum drier. These catalysts were characterized by ^{31}P NMR (Fig. 1) and IR (Fig. 2) spectra, respectively. The ^{31}P NMR spectra of **1a**–**8a** in DMF showed a signal peak at $\delta = -14.5$ ppm which corresponds to the ^{31}P NMR chemical shift of the 12-phosphotungstic acid (Fig. 1a). All the IR spectra of the catalysts showed characteristic skeletal vibrations of the Keggin structure, [ν(P–O) 1080–1085 cm^{-1}, ν(W = O) 977–987 cm^{-1}, ν(W–Ob–W) 895 cm^{-1}, ν(W–Oc–W) 813 cm^{-1}][7,8,10], compared with 12-phosphotungstic acid (Fig. 2a). Our data suggest that the Keggin structure of the 12-phosphotungstic acid was still retained in the 12-phosphotungstate through the synthesis.

3.2. The catalytic oxidation of alcohols

The catalytic activities of these catalysts were compared during the solvent-free oxidation of octan-2-ol at 363 K and the results are given in Fig. 3. It can be seen from Fig. 3 that all these 12-phosphotungstate catalysts have catalytic activities for the oxidation of octan-2-ol. Catalysts **2a**, **3a**, and **4a**, which consisted of short-chain alkylammonium cations, showed low catalytic activities and a yield lower than 30%. The yield of 20% was obtained with catalyst **a**. These catalysts had a lower utilization efficiency of hydrogen peroxide, and most of the hydrogen peroxide was decomposed in the reaction. Therefore, we synthesized catalysts **1a**, **5a**,