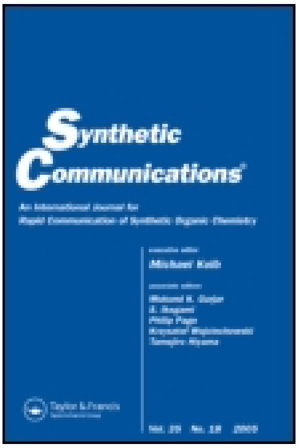

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Lacunary Derivative $[HPW_9O_{34}]^{8-}$ as Reusable and Active Catalyst for Alcohol Oxidation in Water

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LACUNARY DERIVATIVE $[HPW_9O_{34}]^{8-}$ AS REUSABLE AND ACTIVE CATALYST FOR ALCOHOL OXIDATION IN WATER

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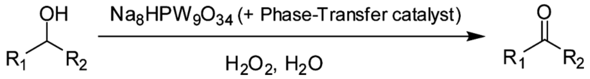
GRAPHICAL ABSTRACT



Abstract *An effective and reusable catalytic system for the oxidation of alcohols was developed based on* $\triangle$-$Na_8HPW_9O_{34}$. *The oxidation was conducted in water using hydrogen peroxide as oxidant. Good yields of ketones were obtained in oxidation of secondary alcohols, and the catalyst was recycled 10 times without obvious loss in activity.*

Keywords Alcohol; catalysis; heteropolyoxotungstate; oxidation; recyclable

INTRODUCTION

The selective oxidation of alcohols to the corresponding carbonyl compounds is an active field of research. From the viewpoint of green chemistry, hydrogen peroxide used as oxidant in liquid-phase oxidation has attracted much attention. It is much cheaper and safer than other peroxides or peracids.[1,2] Polyoxometalates recently have been shown to be active for the selective oxidation. Many catalytic systems for alcohol oxidation with hydrogenperoxide have been disclosed, such as $[(n\text{-}C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$,[3] $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[MoO(O_2)_2]_4\}$,[4] tetrakis(diperoxotungsto)phosphates,[5] lacunary polyoxotungstate of $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$,[6] sodium tungstate + quaternaryammoniumhydrogen sulfate,[7] $[PW_{11}O_{39}]^{7-}$,[8] $[NaP_5W_{30}O_{110}]^{14-}$,[9] and $K_8\,[\gamma\text{-}SiW_{10}O_{36}]\cdot 13H_2O$.[10] Some of these systems use poisonous organic solvents, and in other cases, the recovery of the catalysts was difficult or not mentioned.

Shelden et al.[11,12] found that a water-soluble palladium-phenanthroline catalyst may be used in water for liquid alcohol oxidation. The catalyst could be recycled from the product by separation of the aqueous phase. However, this system

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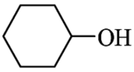
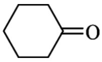
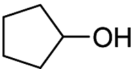
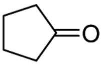
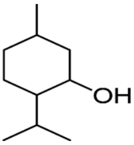
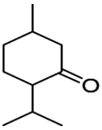
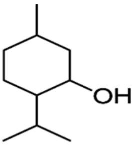
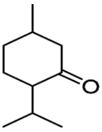
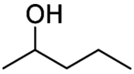
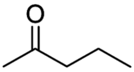
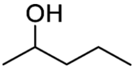
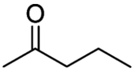
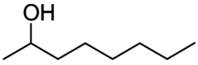
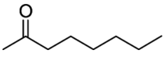
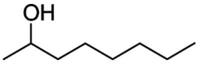
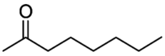
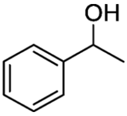
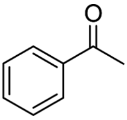
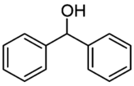
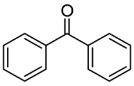
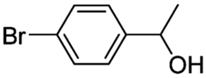
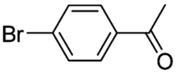
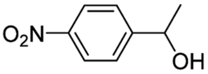
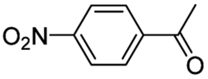
required expensive noble metal and a water-soluble organic ligand. Subsequently, the "self-assembled" catalyst of Na_{12}-$[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ has been investigated as an active catalyst for alcohol oxidation by Neumann.[13–15] This sandwich-type polyoxometalate was an effective and recyclable catalyst for alcohol oxidation in water. The catalyst was used over three reaction cycles without discernible loss in activity or selectivity.

Here, we report an environmentally friendly and efficient procedure for the secondary alcohol oxidation catalyzed by $\triangle$-$Na_8HPW_9O_{34}$ in water with aqueous hydrogen peroxide. Good yields of ketones were obtained, and the catalyst was recycled 10 times without obvious loss in activity or selectivity.

RESULTS AND DISCUSSION

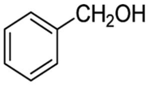
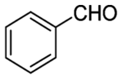
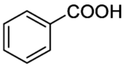
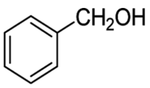
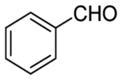
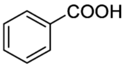
It would be very advantageous for practical applications if the catalyst could be effective and recyclable for the oxidation of alcohols. Table 1 summarizes the catalytic oxidation of various alcohols by the catalyst with 30% H_2O_2. Secondary alcohols including cyclic alcohols, linear alcohols, α-phenylethyl alcohol and benzhydrol were all selectively oxidized to the corresponding ketones in good yields. Several trends may be noted. Cyclohexanol, cyclopentanol, and α-phenylethyl alcohol were effectively converted to the corresponding ketones in water. For other alcohols, the sodium of this tungstophosphate dissolved in water without phase-transfer catalyst was not active enough. Poor yield (only 5%) of the product was detected in the oxidation of racemate (DL)–menthol after 10 h. When cetylpyridinium chloride was added to the system, good yield of 83% of menthone was obtained in 7 h. There is an obvious effect of the hydrophobicity of the substrate. The poor water solubility of DL–menthol meant that the substrate was not well touched with the catalyst in water, but the cation of cetylpyridinium allowed the oxidant of H_2O_2 to react well with the catalyst and substrate. This phenomenon was also present in the oxidation of linear alcohols. For example, the yield of 2-octanone in the oxidation of 2-octanol was only 35% in 10 h, but a good yield of 96% after 6 h was obtained by adding cetylpyridinium chloride. The experimental results also show that the shorter linear alcohol (2-pentanol) was more active than the longer one (2-octanol) in this oxidation system. Besides, the solid alcohol of benzhydrol was also completely oxidized to the corresponding ketone with the help of the phase-transfer catalyst. The substituent secondary alcohols of 4-bromo-α-phenylethyl alcohol and 4-nitro-α-phenylethyl alcohol were used to check the activity of the catalyst. Although they were more difficult to oxidize than α-phenylethyl alcohol, good yields of the corresponding ketones were obtained based on the catalyst within 8 h (Table 1, entries 11 and 12). The representative primary alcohol of benzyl alcohol was also used for the oxidation based on the catalyst. It was found that benzyl alcohol could be successfully oxidized with high conversion (99%) in our catalytic system. However, the product for the oxidation of benzyl alcohol was not the only one. Benzaldehyde and benzoic acid were obtained together. In the previous system reported by Venturello et al., [3] benzonic acid was nearly the sole product (aldehyde was less than 3%). In our catalytic system, the selectivity of benzaldehyde was 24% in the oxidation of benzyl alcohol with hydrogen peroxide, which was different from the previous report. A combination of H_2O_2/urea mixture as the oxidant was tried to avoid the overoxidation of benzaldehyde. The

Table 1. Oxidation of various alcohols catalyzed by $\triangle$-$Na_8HPW_9O_{34}$ with H_2O_2[a]

Entry	Substrate	Product	Time (h)	Yield (mol%)	Selectivity (mol%)
1			6	99	99
2			8	97	99
3			10	5	99
4[b]			7	83	99
5			10	74	98
6[b]			6	97	98
7			10	35	98
8[b]			6	96	98
9			5	94	99
10[b]			7	99	99
11			8	78	99
12			8	85	99

(*Continued*)

Table 1. Continued

Entry	Substrate	Product	Time (h)	Yield (mol%)	Selectivity (mol%)
13			8	24	24
			8	75	76
14[c]			8	31	56
			8	24	44

[a] Reaction conditions: 7 μmol catalyst, 2 ml water, 1 mmol alcohol, 5 mmol (30% aq.) H_2O_2; reaction temperature: 85 °C. The selectivity was based on ketone. Yields and selectivities were determined by gas chromatography using an internal standard technique.

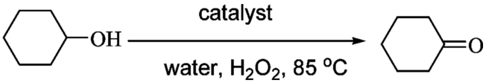
[b] 10 mg cetylpyridinium chloride were added.

[c] H_2O_2/urea (1:1) as the oxidant.

selectivity of benzaldehyde reached 56%, but the conversion of benzyl alcohol was decreased to 55%.

The catalyst of Δ-$Na_8HPW_9O_{34} \cdot 19H_2O$ is a water-soluble catalyst. In this biphasic system, the catalyst is dissolved in water and oxidized alcohols. After the reaction, the organic products were separated from the aqueous phase by extraction and the organic phase was taken for analysis. The aqueous phase containing the

Table 2. Oxidation of cyclohexanol by catalyst for different cycles[a]



Cycles	Yield (mol%)	Selectivity (mol%)
1	99	99
2	99	99
3	99	99
4	99	99
5	97	99
6	97	99
7	97	99
8	98	99
9	98	99
10	97	99

[a] Reaction conditions: 0.028 mmol catalyst, 10 ml water, 4 mmol alcohol, 20 mmol (30% aq.) H_2O_2; reaction temperature: 85 °C; reaction time: 6 h.

catalyst could be recycled to do the next oxidation. Because the catalyst was still dissolving in water after extraction, new catalyst and new solvent were not needed for the next cycle. To the aqueous phase, addition of alcohols and H_2O_2 was sufficient for the next oxidation. The catalytic activity in the oxidation of cyclohexanol for different cycles is shown in Table 2. It can be seen that the catalytic activity and selectivity of the reused catalytic system were nearly the same as that of the first oxidation. Even after 10 consecutive cycles of the reaction, 97% yield of the cyclohexanone with 99% selectivity was still obtained in this catalytic system, indicating that this system was a robust and reusable oxidation system.

The fresh catalyst and recovered catalysts were characterized with Fourier transform–infrared (FT-IR) spectra. As shown in Fig. 1, the IR spectrum of $\triangle$-$Na_8HPW_9O_{34} \cdot 19H_2O$ [Fig.1(a)] exhibited characteristic peaks at 1171–994 and 896–742 cm^{-1} that were attributed to ν (P-O) and ν (W-O), respectively.[16] There were obvious differences in the IR spectrum between the fresh catalyst and the catalyst of cycle 1, indicating that the structure of the catalyst after the first reaction was changed. However, when the catalyst was recycled again, we found that the IR spectrum of cycle 2 catalyst was similar to that of cycle 1 catalyst, indicating that

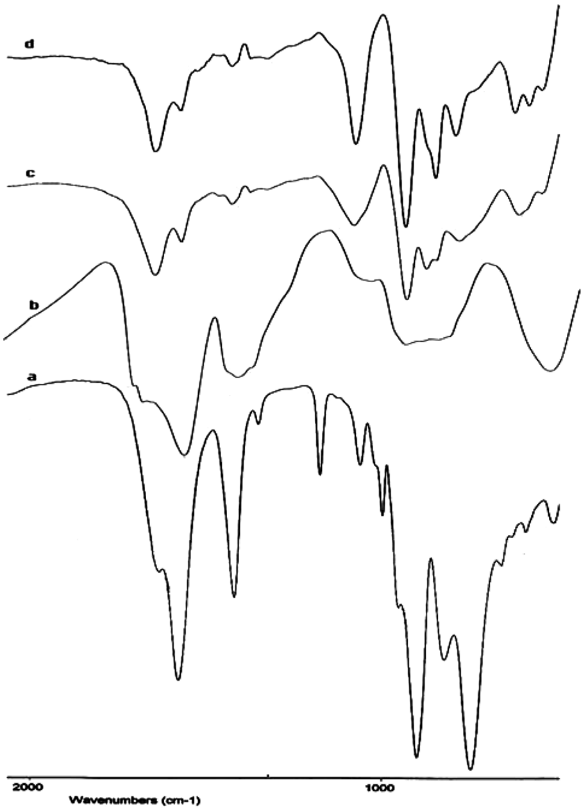
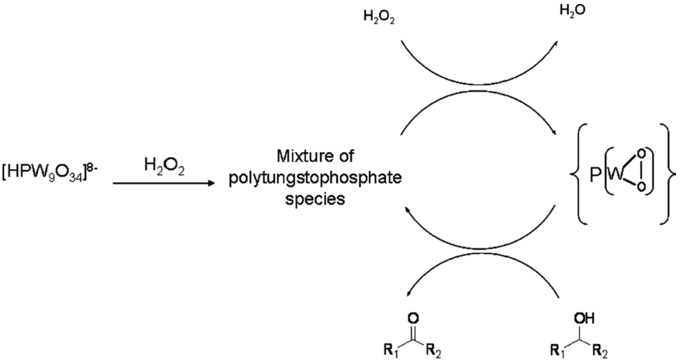


Figure 1. IR spectra of (a) the fresh catalyst of $\triangle$-$Na_8HPW_9O_{34}$; (b) the catalyst with hydrogen peroxide; (c) the catalyst of cycle 1; and (d) the catalyst of cycle 2.



Scheme 1. The possible mechanism for oxidation of alcohols by catalyst $\triangle$-$Na_8HPW_9O_{34} \cdot 19H_2O$.

the structure of the catalyst would not changed after the first cycle. The mixture of the catalyst with hydrogen peroxide was also characterized with the IR spectrum. There is a broad peak in the spectrum at 932–806 cm^{-1}, including three peaks: 932, 888, and 840 cm^{-1}. The IR bands at 1029, 932, and 888 cm^{-1} can be assigned to ν (P–O), ν (W = O), and ν (W–Ob–W) (corner-sharing), respectively.[17,18] The band at 840 cm^{-1} was attributed to ν (O–O), which is responsible for the oxidation. Compared with the activity of the used catalyst showed in Table 2, we proposed a possible mechanism for alcohol oxidation by the catalyst of $\triangle$-$Na_8HPW_9O_{34} \cdot 19H_2O$ in water with hydrogen peroxide (shown in Scheme 1). When the catalyst was treated with hydrogen peroxide, the structure of the catalyst changed into a mixture of polytungstophosphate species. With the effect of H_2O_2, they could be transferred to each other and finally became the true active peroxotungstophosphate species. When the oxidation catalyzed by the active complexes was finished, the catalyst changed back to the mixture of polytungstophosphate species.

In summary, we demonstrated a water-soluble recyclable catalytic system in the oxidation of alcohols with hydrogen peroxide. Secondary alcohols were selectively oxidized to the corresponding ketones in good yields. The catalyst was reused for 10 cycles without loss in activity. This system is an environmentally friendly and reusable oxidation system for alcohol oxidation.

EXPERIMENTAL

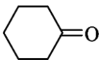
Preparation of the Catalyst $\triangle$-$Na_8HPW_9O_{34} \cdot 19H_2O$[16]

First 30 g of Na_2 $WO_4 \cdot 2H_2O$ were dissolved in 37 ml of distilled water with stirring. Then 0.75 ml of 85% H_3PO_4, followed by 5.5 ml of glacial acetic acid, were added to the stirring solution. After a few seconds, the solution became cloudy and after about 1 min a heavy white precipitate had formed. The solid was collected and first dried under aspiration for 24 h, and then the aspirated solid was left in the air for 24 h. After that, the solid was dried at 140 °C for about 1.5 h. The yield of $\triangle$-$Na_8HPW_9O_{34} \cdot 19H_2O$ was about 80%. IR spectrum (KBr, cm^{-1}): 1171, 1057, 994, 947, 896, 818, 742, 653, 624, 588, 507, 470, 417.

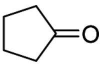
Catalytic Reaction

The catalytic reactions were performed in a 25-ml, two-necked, round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. The oxidations were carried out in the following procedure: catalyst (7 μmol), water (2 ml), substrate (1 mmol), and H_2O_2 (5 mmol, 30% aq.) were charged in the reaction flask. The reaction was carried out at 358 K. When the reaction was over, the organic products were separated from the aqueous phase by extraction, and then the organic layer was analyzed by gas chromatography (GC) with the internal standard method. After separation, addition of alcohols (1 mmol) and H_2O_2 (30% aq.) to the aqueous phase containing the catalyst was carried out for the next oxidation. Assignments of products were made by comparison with authentic samples based on retention time in GC. Selected samples were also analyzed by NMR.

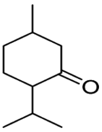
Data



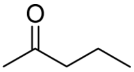
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 125 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 2.3 min.



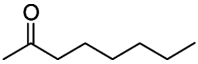
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9 AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 130 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 2.2 min.



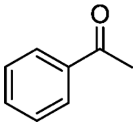
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9 AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 135 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 3.7 min.



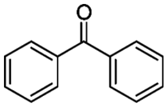
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9 AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 85 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 2.7 min.



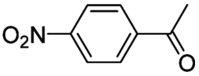
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9 AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 130 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 2.4 min.



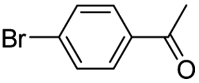
GC (FFAP capillary column, 30 m × 0.32 mm × 0.5 μm, GC-9 AM, Shimadzu Corporation) carrier gas: N_2, 1.2 kg/cm^2, column temperature: 155 °C, injection temperature: 200 °C, detection temperature: 200 °C, and retention time: 4.0 min.



The pure product was obtained by distillation or silica-gel column chromatography. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.80 (4H, d d, J = 8.4, 1.2 Hz), 7.59 (2H, m), 7.48 (4H, m). ^{13}C NMR (100 MHz; $CDCl_3$) δ 197.7, 138.6, 133.38, 131.0, 129.2.



^{1}H NMR (400 MHz; $CDCl_3$) δ 8.23 (4H, d, $J = 8.8$ Hz), 8.06 (2H, d, $J = 8.8$ Hz), 2.64 (3H, s). ^{13}C NMR (100 MHz; $CDCl_3$) δ196.17, 150.14, 141.26, 129.12, 123.61, 26.73.



^{1}H NMR (400 MHz; $CDCl_3$) δ 7.78 (2H, d, $J = 8.5$ Hz), 7.57 (2H, d, $J = 8.4$ Hz), 2.55 (3H, s). ^{13}C NMR (100 MHz; $CDCl_3$) δ 196.80, 135.76, 131.77, 129.73, 128.16, 77.32, 77.00, 76.68, 26.39.

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