New active and recyclable catalytic systems based on $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ for alcohol oxidation with hydrogen peroxide in water

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Abstract: A "sandwich" type tungstophosphate, $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, was used as the efficient and reusable catalyst for alcohol oxidation. The catalyst I of $K_{10}Zn_4(H_2O)_2(PW_9O_{34})_2 \cdot 20H_2O$ and the catalyst II of $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2[Zn_4(H_2O)_2(PW_9O_{34})_2]$ were used to catalyze the oxidation of alcohols in water. High yields of the

corresponding carbonyl compounds were obtained. The catalysts were recycled several times without loss in activity.

Key words: polyoxometalate, recyclable, catalyst, oxidation, alcohol.

Résumé : On a utilisé un tungstophosphate de type « sandwich », $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ comme catalyseur efficace et réutilisable pour l'oxydation d'alcools. On a utilisé les catalyseurs I, de formule $K_{10}Zn_4(H_2O)_2(PW_9O_{34})_2$ ·20H₂O, et II, de formule $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2$ $[Zn_4(H_2O)_2(PW_9O_{34})_2]$, pour catalyseur l'oxydation d'alcools dans l'eau. On a obtenu des rendements élevés des dérivés carbonylés correspondants. Les catalyseurs ont été recyclés plusieurs fois sans perte d'activité.

Mots-clés : polyoxométalate, recyclable, catalyseur, oxydation, alcool.

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Introduction

Carbonyl compounds are important precursors of various chemicals.¹⁻³ The selective oxidation of alcohols to the corresponding carbonyl compounds is an active field of research. Hydrogen peroxide used as the oxidant in liquidphase oxidation has attracted much attention from researchers from the viewpoint of green chemistry. It overcomes the disadvantage of the toxic traditional inorganic oxidants,⁴ and it is much cheaper and safer than other organic peroxides or peracids.⁵ Polyoxometalates as effective catalysts for oxidation reactions have attracted wide attention in the past. Most examples of alcohol oxidation with hydrogen peroxide employed polyoxometalates as catalysts and have been reported, e.g., $[(n-C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}, 6 [\pi C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[MoO(O_2)_2]_4\},^7$ tetrakis(diperoxotungsto)phosphates,8 lacunary polyoxotungstate of [y- $SiW_{10}O_{36}(PhPO)_2]^{4-,9}$ sodium tungstate + quaternaryammoniumhydrogen sulfate,¹⁰ [PW₁₁O₃₉]^{7-,11} [NaP₅W₃₀O₁₁₀]^{14-,12} and so on. However, in these catalytic systems, the use of chlorocarbon poisonous solvents or the difficult recovery and reuse of those catalysts has restricted their wide applications in industrial and laboratorial synthesis.

From the viewpoint of green chemistry, water as an excellent solvent used in the catalytic oxidation of alcohols has received much attention recently. Although a number of methods have been developed,^{13–19} the search for effective, new, environmentally benign, and reusable procedures for alcohol oxidation still remains an important challenge.

To the best of our knowledge, the "sandwich" type tungstophosphate, [Zn₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻, has not been reported on the catalytic activity for the oxidation of alcohols in water. We report here two new catalytic systems for alcohol oxidation using it as a recyclable and active catalyst with hydrogen peroxide in water. (i) The potassium of the tungstophosphate $(K_{10}Zn_4(H_2O)_2(PW_9O_{34})_2 \cdot 20H_2O)$ was used to oxidize several alcohols in water with hydrogen peroxide. The catalyst was reused for the next cycle from the organic product by separation of the aqueous phase. There was no discernable loss in activity and selectivity even after 10 cycles. (ii) High yields of ketones were obtained in the oxidation of secondary alcohols in water using $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2[Zn_4(H_2O)_2(PW_9O_{34})_2]$. The catalyst was separated from the reaction mixture by adding diethyl ether to the system after the reaction. Comparing previous reports, there are some advantages in using our system: (i) water (a green solvent) was used as the solvent in the oxidation, (*ii*) the active catalysts could be easily reused, and (*iii*) some solid alcohols like DL-menthol and benzhydrol were

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also successfully oxidized with excellent yields in our catalytic system.

Experimental

Reagents

All chemicals were analytical grade, commercially available, and used without further purification unless otherwise stated.

Preparation of catalysts

The potassium of the sandwich type tungstophosphate, $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (catalyst I), was synthesized by the procedure reported in ref. 20. The catalyst II of $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2[Zn_4(H_2O)_2(PW_9O_{34})_2]$ was obtained from K₁₀Zn₄(H₂O)₂(PW₉O₃₄)₂·20H₂O by the following procedure: 0.9 g of K₁₀Zn₄(H₂O)₂(PW₉O₃₄)₂·20H₂O was dissolved in 55 mL of water. To this solution, 0.9 g of dioctadecyl dimethyl ammonium chloride dissolved in 10 mL of tert-butyl alcohol was added slowly. The mixture was stirred vigorously for 4 h at 40 °C. A white solid was filtered off and then washed with an excess amount of 97%. water. The vield was Anal. calcd. for $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2[Zn_4(H_2O)_2(PW_9O_{34})_2]$: C 39.51, H 6.97, N 1.21, P 0.67, W 35.84, Zn 2.82; found: C 40.68, H 6.98, N 1.13, P 0.60, W 35.23, Zn 2.74.

Characterization techniques

Infrared spectra were recorded on a Nicolet FTIR-360 FTIR spectrometer. The catalysts were measured using 2%–4% (*w/w*) KBr pellets prepared by manual grinding. ³¹P MAS NMR spectra were recorded at 9.4 T on a Bruker Avance-400 wide bore spectrometer. GC analyses were performed on Shimadzu GC-9AM with a flame ionization detector equipped with a FFAP capillary. Mass spectra were recorded on a Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV and equipped with a DB-5 capillary column. Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (IRIS ER/S), and C, H, and N contents were measured on a German Elementar Vario EL spectrometer.

Catalytic reaction

The oxidation was carried out in two procedures. Procedure A: catalyst I of $K_{10}Zn_4(H_2O)_2(PW_9O_{34})_2 \cdot 20H_2O$ (9 μ mol), water (3 mL), substrate (1 mmol), and H₂O₂ (5 mmol, 30% aq) were added to the reaction flask at 363 K. When the reaction was over, the organic products were separated from the aqueous phase by extraction. Then, readdition of alcohols (1 mmol) and H_2O_2 (30% aq) to the aqueous phase containing the catalyst were carried out for the next oxidation. Procedure B: catalyst II of $[(C_{18}H_{37})_2(CH_3)_2N]_8K_2[Zn_4(H_2O)_2(PW_9O_{34})_2] \quad (18)$ μmol), substrate (4 mmol), and H_2O_2 (20 mmol, 30% aq) were added to the reaction flask. The reaction was carried out at 363 K. When the reaction was over, the catalyst precipitated with cooling and was collected completely from the solution by adding diethyl ether to the system. Assignments of products were made by comparison with authentic samples. Selected samples were also analyzed by GC-MS (Finnigan Trace DSQ), and some isolated products were characterized by NMR.

Results and discussion

Table 1 summarizes the catalytic oxidation of various alcohols with 30% H₂O₂ by catalyst I and II in procedures A and B, respectively. High yields of ketones were obtained in the oxidation of cyclohexanol and cyclopentanol in both procedures. For DL-menthol, a low yield of 8% was detected using procedure A after 10 h. However, a high yield of menthone (97%) was obtained using procedure B after 6 h. This difference should be attributed to whether the catalyst could be in good contact with the substrates during the oxidation. In procedure A, the poor water solubility of DL-menthol resulted in the substrate not being in good contact with the catalyst dissolving in water. But in procedure B, the cation of dioctadecyl dimethyl ammonium promoted the contact between the aqueous phase and the substrate. So, there were obvious differences between procedures A and B during the oxidation of these hydrophobic alcohols. This phenomenon was also presented in the oxidation of linear alcohols. For the oxidation of *sec*-butyl alcohol, 2-pentanol, and 2-octanol, the reaction time in procedure B was shorter than that in procedure A, but the activity of catalyst II in procedure B was much higher than that of catalyst I in procedure A. This was especially true for 2-octanol; the yield of 2-octanone in procedure A was only 39% in 10 h, but a high yield of 99% was obtained in procedure B after 6 h. Even so, procedure A based on catalyst I is actually an active catalytic system for most of the substrates listed in Table 1. Benzhydrol and 1-phenylethanol were oxidized to their corresponding ketones with high yields using procedure A, producing similar results with procedure B. For a more active substrate (1phenylethanol), a two molar excess of H₂O₂ using catalyst I in water was sufficient (not listed here). Interestingly, catalyst I was also active for the primary alcohol of benzyl alcohol, and the products of benzaldehyde and benzoic acid were obtained, respectively, in high yields by controlling the amount of H_2O_2 in the system. Benzaldehyde is a very important chemical that has widespread applications in the fields of flavors, odorants, and pharmaceutical intermediates.²¹ Therefore, we tried to get benzaldehyde from the oxidation of benzyl alcohol in our system. When the ratio of H₂O₂-substrate was 1:2, benzaldehyde as the sole product with a 94% yield was obtained using catalyst I in water. Increasing the amount of hydrogen peroxide to a molar excess five times greater than the substrate, the conversion of benzyl alcohol reached up to 100%, but benzoic acid as the main product was obtained with 93% selectivity. The results indicated that increasing the amount of hydrogen peroxide enhanced the activity of oxidation, but the excessive oxidant would also bring in deep oxidation.

 $K_{10}Zn_4(H_2O)_2(PW_9O_{34})_2\cdot 20H_2O$ is a "water-soluble" catalyst, and it effectively catalyzes the oxidation of alcohols in water. After reaction, the organic products were separated from the aqueous phase by extraction. The aqueous phase containing the catalyst could be kept to do the next oxidation. The catalytic results in the oxidation of cyclohexanol on catalyst I for different cycles are shown in Fig. 1. It can be seen that the activity of the reused catalyst did not

Entry	Substrate	Product	Procedure	Time (h)	Yield (mol%)	Selectivity (mol%)
1	—ОН	0	А	6	99	99
2	—ОН	0	В	6	99	99
3	ОН	0	А	8	90	99
4	ОН) =0	В	8	99	99
5	Сн	, , ,	А	10	8	98
6	ОН		В	6	97	98
7	ОН	O V	А	9	97	99
8	OH	0	В	5	98	99
9	OH	o IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	А	10	88	99
10	OH	0	В	5	98	99
11	OH	0	А	10	39	99
12	OH	0	В	6	99	99
13	OH C	O C	А	3	99	99
14	OH	° C	В	3	99	99
15	OH		А	8	99	99
16	OH		В	6	99	99
17	CH ₂ OH	СООН	А	7	93	93
18 ^{<i>a</i>}	CH ₂ OH	СНО	А	8	94	99

Table 1. Oxidation of various alcohols catalyzed by $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ with H_2O_2 .

Note: Reaction conditions: Procedure A: 9 μmol catalyst I; 3 mL water; 1 mmol alcohol; 5 mmol (30 % aq) H₂O₂. Procedure B: 18 μmol catalyst I; 4 mmol alcohol; 20 mmol (30 % aq) H₂O₂; reaction temperature: 90 °C. The selectivity was based on ketone, aldehyde, or acid. ^{*a*} 9 μmol catalyst I; 3 ml water; 2 mmol alcohol; 1 mmol (30 % aq) H₂O₂, the yield was based on H₂O₂; the selectivity was based on benzaldehyde.

change. Even after 10 consecutive cycles of the reaction, a 97% yield of the cyclohexanone with 99% selectivity was still kept in this catalytic system, indicating that this system is a robust and reusable oxidation system.

To evaluate the reusable property of catalyst II, the oxidation system in procedure B was investigated. The countercation of dioctadecyl dimethyl ammonium made the catalyst disperse in the mixture to form an emulsion with heating. After the reaction finished with the temperature dropping, the system changed to turbid. Then, some diethyl ether was added to the system to precipitate the catalyst completely. The catalyst was recovered by centrifugation and used for the next cycle. Table 2 shows the oxidation of 2-octanol using procedure B for different cycles. A yield of 98% was Fig. 1. Oxidation of cyclohexanol by catalyst I in procedure A for different cycles. Reaction conditions were similar to that in Table 1. Fig. 3. ³¹P MAS NMR spectra of the two catalysts before and after an oxidation reaction: (a) fresh catalyst I, (b) used catalyst I, (c) fresh catalyst II, and (d) used catalyst II.



Table 2. Oxidation of 2-octanol by catalyst II for different cycles.

Catalyst	Yield (mol%)	Selectivity (mol%)
Fresh	98	99
Cycle 1	98	99
Cycle 2	97	99
Cycle 3	98	99

Note: Reaction conditions were the same as for procedure B.

Fig. 2. IR spectra of the two catalysts before and after oxidation reaction: (a) fresh catalyst I, (b) used catalyst I, (c) fresh catalyst II, and (d) used catalyst II.



kept after three cycles, indicating that this catalytic system based on catalyst II is also a recyclable oxidation system.

The fresh catalysts and the used ones were characterized with FTIR spectra. As shown in Fig. 2, the IR spectrum of



16



the fresh catalyst K₁₀Zn₄(H₂O)₂(PW₉O₃₄)₂·20H₂O (Fig. 2a) exhibited characteristic peaks at 1034, 942, 886, and 756 cm⁻¹ and were similar to the reference reports.²⁰ The single band at ~1034 cm⁻¹, near the P–O band position (1080 cm⁻¹) of $[PW_{12}O_{40}]^{3-}$, suggests that significant restoration of tetrahedral symmetry to the phosphate group has

occurred on metal substitution. There were obvious differences between the IR spectra of the fresh catalyst I and the used one. Several peaks were moved to new positions at 1054, 955, 889, 831, and 762 cm⁻¹, indicating that the structure of the catalyst has changed. It was not surprising that it could be ascribed to the recovery method of the catalyst. There have been several papers^{16,22} that reported that the alteration of polyoxotungstate catalyst in the presence of H_2O_2 followed by the recovery of the initial structure after evaporation of solvents has always taken place, and the change of the structures cannot be ruled out. Considering the activity of the used catalyst, the fresh catalyst of K₁₀Zn₄(H₂O)₂(PW₉O₃₄)₂·20H₂O seems to act as a precatalyst, which then maintains the catalytic activity during the later cycles. The IR spectra of the fresh catalyst II and the used one are also shown in Fig. 2; the peaks at 2919 and 2850 cm⁻¹ were attributed to the C-H bonds of the quaternary ammonium cation of catalyst II. The peaks at 1033, 933, and 881 cm⁻¹ were similar to that of catalyst I. Those revealed that catalyst II was synthesized containing a sandwich type tungstophosphate joined with the quaternary ammonium cation. The IR spectrum of the used catalyst II (Fig. 2d) was similar to the fresh one (Fig. 2c) except that some intensities of the peaks changed. There were no obvious changes between the fresh catalyst II and the used one.

This phenomenon was consistent with the ³¹P MAS NMR characterization of the catalysts. As shown in Fig. 3, the strong peak at -4.7 ppm in Fig. 3a could be attributed to the sandwich type tungstophosphate structure of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, which was very different from the structure of the keggin polytungstophosphate of $[PW_{12}O_{40}]^{3-}$ at about -15.8 ppm.^{23,24} There were obvious changes shown in Fig. 3b of the used catalyst I; new peaks at 1.0 and -11.9 ppm appeared, which might be attributed to other keggin structures of polytungstophosphate. The structure of the catalyst has changed during the recovery course by evaporation of H_2O_2 aqueous solution. The ${}^{31}P$ MAS NMR of the fresh catalyst II kept the original structure of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (shown in Fig. 3c) at -5.0 ppm. After oxidation, the main species was also the sandwich type structure. Other peaks at 4.3, -12.4, and -15.3 ppm should be different kinds of polytungstophosphate species, which were obtained during the reaction with hydrogen peroxide. The original structure of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ that could be kept in the used catalyst II might be attributed to the solvent precipitation recovery method of the catalyst. In addition, the countercation of the catalyst was also an important factor in this behavior. The countercation of catalyst II could prevent the change of the catalyst during the reaction, and the different amount of water in the reaction conditions might also play an important role.

Conclusions

In summary, we have demonstrated two new active and recyclable catalytic systems based on a sandwich type tungstophosphate, $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, for alcohol oxidation with hydrogen peroxide in water. Secondary alcohols were selectively oxidized to the corresponding ketones with high yields. Benzyl alcohol was converted to benzaldehyde at a high conversion rate and selectivity by controlling the amount of H_2O_2 . The catalysts were recycled several times without an obvious loss in activity. These catalytic systems are environmentally friendly and practical systems for alcohol oxidation.

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