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ORIGINAL PAPER

Highly selective oxidation of alcohols with hydrogen peroxide and polyethylene oxide-supported long-chain imidazolium polyoxometalate hybrid catalyst

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Abstract A polyethylene oxide-supported long-chain imidazolium polyoxometalate hybrid catalyst ([PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$) was synthesized and employed as catalyst for the oxidation of various alcohols with H_2O_2 at room temperature. Owing to the exsistence of long chain, the catalyst had a good surface-active performance. The catalyst showed high activity not only in the oxidation of primary and secondary benzylic alcohols but also in the oxidation of heterocyclic and allylic alcohols to give good yields of aldehydes or ketones. The catalyst can be reused for six times without significant loss of its activity.

Keywords [PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ · Hybrid catalyst · Oxidation of alcohols · Room temperature

Introduction

The selective oxidation of primary and secondary alcohols into the corresponding aldehydes or ketones is one of the most important and challenging transformations for many biological and organic reactions providing key intermediates and valuable pharmaceuticals [1–3]. Large variety of traditional methods employing chemical reagents in stoichiometric amounts have been reported to accomplish this transformation with considerable drawbacks, such as use of expensive reagents and volatile organic solvents, and discharge of environmentally pernicious wastes [4, 5]. From an economical and environmental viewpoint, the development of catalytic oxidation systems with cheap and green oxidants, such as molecular oxygen or hydrogen peroxide is particularly attractive and many efforts have been devoted to the development of efficient procedures over the last years. These attractive catalytic systems display high atom economy and release only innocuous by-products such as H_2O [6–10].

Selective oxidation of organic substrates with polyoxometalates (POMs)-based systems is of great importance in industry and are widely used for manufacturing various high-demand commodity chemicals. Recently, organic hybrids of POMs are attractive catalyst for various oxidation reactions. Examples which include surfactant-POM combination [11, 12], coordination polymers [13, 14], polymer-POM conjugates [15–17], and POM-ILs [18–23] have been prepared and tested as promising catalysts for the oxidation process.

In this work, we report a novel imidazolium polyoxometalate composite in which peroxotungstate is immobilized onto polyethylene oxide supported long alkyl chain ionic liquids (Fig. 1). Owing to the existence of the polyethylene oxide and long alkyl chain moiety, both improved catalytic performance, easy separation and excellent recoverability were achieved. The protocol presented here provides an efficacious strategy to achieve both catalysts recycling and product isolation from a viewpoint of green chemistry.

Results and discussion

The catalysts could be easily prepared in a four-step procedure. First, polyethylene glycol was treated with thionyl chloride in anhydrous toluene at 0 °C under an inert gas

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for 24 h to afford PEO-dichloride. PEO-dichloride was subsequently added to sodium imidazole salts in toluene at 80 °C for 24 h to generate the PEO-diimidazolium. Then, PEO-diimidazolium was reacted with 1-bromododecane $C_{12}H_{25}Br$ at 70 °C for 20 h to give PEO-didodecylimidazolium. In the next step, the PEO-didodecylimidazolium was then treated with $H_3[PW_{12}O_{40}]$ in dry ethanol at 40 °C for 6 h. The $[\text{PEO-diimidazolium}]_3[PW_{12}O_{40}]_2$ was obtained as a white viscous solid (Scheme 1).

Figure 2 showed the IR spectra of $[\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$, (PEO-didodecylimidazolium and $H_3PW_{12}O_{40}$ raw material, respectively. IR spectrum of PEO-didodecylimidazolium(curve a) and $[\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$ (curve c) showed detectable changes that were characteristic of C–O–C stretching vibrations in around 1100 cm^{-1} C–H stretching vibrations around 2800 cm^{-1}. The characteristic peaks that belong to $H_3PW_{12}O_{40}$ around 1079–1040 cm^{-1} v(P–O), 945 cm^{-1} v(W=O), and 900–725 cm^{-1} v(W–O–W) were exhibited clearly in its Keggin structure (curve b). For $[\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$, minor difference could be detected when compared the IR spectrum of catalyst $[\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$ with that of $H_3PW_4O_{12}$. In spite of the decrease of peak intensities and slight shift of peak positions, the characteristic peaks appeared distinctively, which indicated that the salts retained the well Keggin structure even after protons in $H_3PW_{12}O_{40}$ were substituted by organic cations.

With benzyl alcohol as the model substrate, the catalyst $\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$ was designed for the oxidation of alcohols. The exploratory experiments were started by screening the heteropoly acid salts. The

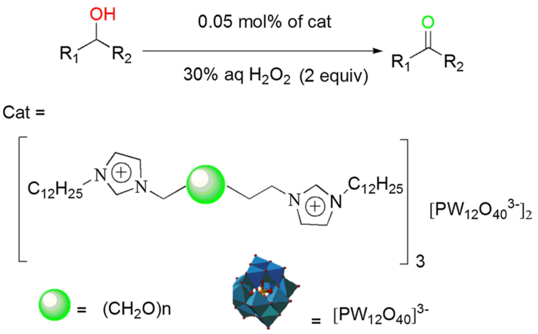


Fig. 1 Selective oxidation of alcohols with hydrogen peroxide catalyzed by $[\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$

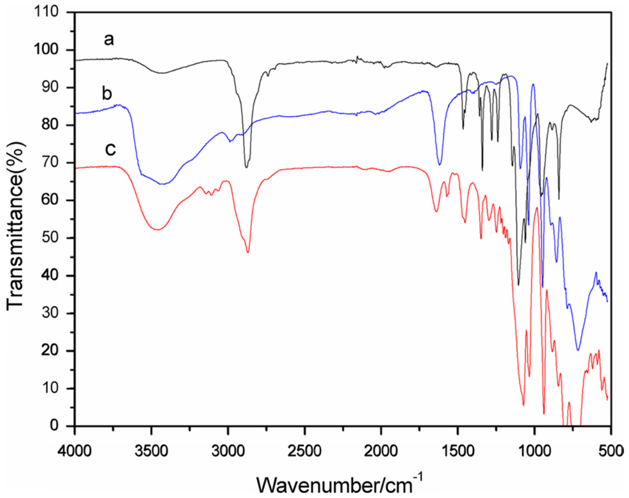
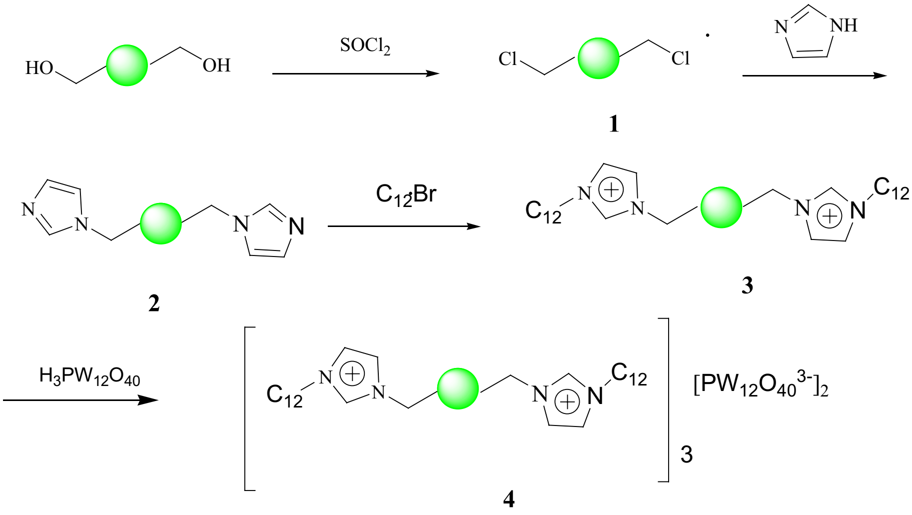


Fig. 2 IR spectra (*a*) PEO-didodecylimidazolium (*b*) $H_3PW_{12}O_{40}$ (*c*) $\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$



Scheme 1 Synthesis of $\text{PEO-didodecylimidazolium}]_3[PW_{12}O_{40}]_2$

results are summarized in Table 1, entries 1-3. It is found that phosphotungstic acid gave best performance for the oxidation of benzyl alcohol. Possible reason was that tungstic ion was easier to form polyoxometalate which was the main active species in the process of oxidation of alcohols. The lengths of carbon chain also have a great impact on oxidation of alcohols. The results using different lengths of carbon chain are summarized in Table 1. It was obviously found that the advantage effect appeared with increase of the length of carbon (n = 4, 8, 12), which may attribute to stronger lipophilic ability and better surface-active performance, but the conversion and yield have no obvious increase when the number of carbon atom exceeded $n = 12$ (Table 1, entries 3–7).

Table 1 Screening of catalysts for oxidation of benzyl alcohol

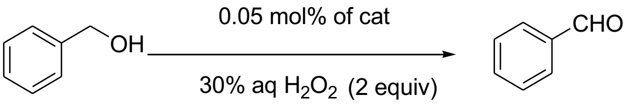
Entry	Heteropoly acid	C_nH_{2n+1}	Conv (%)	Yeild (%)
1	Phosphotungstic acid	$n = 12$	100	98
2	Phosphomolybdic acid	$n = 12$	69	64
3	Molybdovanadophosphoric acid	$n = 12$	60	55
4	Phosphotungstic acid	$n = 0$	50	48
5	Phosphotungstic acid	$n = 4$	65	64
6	Phosphotungstic acid	$n = 8$	89	85
7	Phosphotungstic acid	$n = 16$	100	98

Table 2 Oxidation of benzyl alcohol under different surfactant conditions

Entry	Surfactant	Conv (%)	Yeild (%)
1	PEO-didodecylimidazolium	100	98
2	CTAB	90	85
3	SDS	59	56
4	TX-10	70	67

In order to investigate the surface-active effect of [PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ upon the reactions, control experiments using different surfacants for oxidations of benzyl alcohol were studied. As can be seen in Table 2, [PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ system gave the best result over cationic surfactant cetyl trimethylammonium bromide(CTAB), acetonitrile, neutral surfactant TritonX-10, anionic surfactant sodium dodecyl sulfate (SDS) (Table 2, entries 1–4). Possible reasons are as follows. Firstly, with attraction of POM anion by cationic surfactant, the conversion rate in cationic surfactant micelles was significantly higher than anionic surfactant under the same conditions. It may be due to strong electrostatic attraction between the imidazolium cation head group on micelle shell and phosphotungstic acid anion ($[PW_{12}O_{40}]^{3-}$), which leads to concentration of $[PW_{12}O_{40}]^{3-}$ in the surface of the micelles significantly and promotes the oxidation reaction effectively. To the contrary, strong electrostatic repulsion exists between the anionic surfactant anionic head group and $[PW_{12}O_{40}]^{3-}$on micelle shell therefore the oxidation reaction was strongly suppressed. Since micelle shell of the nonionic surfactant is uncharged, there is no electrostatic attraction or the electrostatic repulsion between the

Table 3 Reaction conditions on oxidation of benzyl alcohol under micelle conditions^a



Entry	Catalysts (mol %)	H_2O_2 (equiv)	T/ °C	Conv (%)^a	Yeild (%)^b
1	–	3	rt	–	–
2	TPA(0.05)	2	rt	80	75
3	PEO-didodecylimidazolium(0.05)	3	rt	–	–
4	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$(0.05)	2	rt	100	98
5	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.01)	2	rt	89	84
6	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.1)	2	rt	>99	96
7	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.20)	2	rt	>99	96
8	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05)	2	40	99	95
9	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05)	2	60	100	90
10	[PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05)	2	80	100	85

Reaction conditions: benzyl alcohol (10 mmol), [PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05 mol % of benzyl acohol), 30 % aq H_2O_2 (2 equiv), rt

[a] Determined by HPLC

[b] Isolated yield

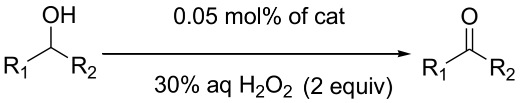
imidazolium cation head group and phosphotungstic acid anion $[PW_{12}O_{40}]^{3-}$, so that the catalytic activity of nonionic surfactant for oxidation was between the cationic surfactant and anionic surfactant.

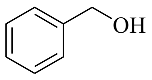
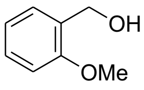
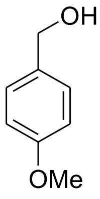
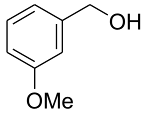
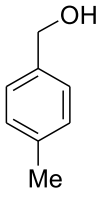
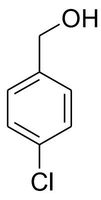
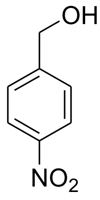
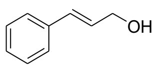
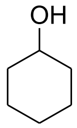
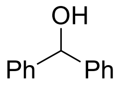
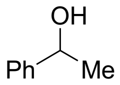
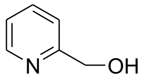
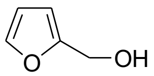
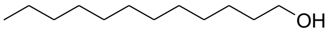
To further optimize the reaction conditions, control experiments were carried out with benzyl alcohol as substrate and H_2O_2 as oxidant. The comparable results were summarized in Table 3. It was found that almost no product was obtained in aqueous solution without catalyst (Table 3, entry 1) or without POMs (Table 3, entry 3). All these facts indicated that it was still Keggion anions that served as the active species for oxidation reactions. The encapsulation process would not change either reaction activity or mechanism (Table 3, entry 2, and entry 4). In addition, catalytic amount was enough to proceed the reaction and the reaction termination could be observed with the removal of it. Further increase of catalyst amount would be meaningless (Table 3, entries 5–7). The reaction was performed well even at room temperature. High temperature obviously accelerates the decomposition of H_2O_2 and decreases the selectivity of benaldehyde (Table 3, entries 8–10).

To examine the utility and generality of this methodology for the oxidation of alcohols, we applied the present system to a variety of alcohols as shown in Table 4. Substrate scope was extended to benzylic, allylic, heterocyclic, and aliphatic alcohols. In all cases, ketones or aldehydes were the only detected products. Obviously, the activities of primary benzylic alcohols were best, and the activities of those primary benzylic alcohols were also not significantly affected by the electronic properties (electron-withdrawing or electron-donating group) and steric hindrance of the substituents on the benzene ring. Secondary alcohols such as benzhydrol and 2-phenylethanol also gave a moderate yield by prolonging the reaction time. It was found that the oxidative efficiency was not affected with the existence of double bond and the double bond remained stable during the oxidation process. Heterocyclic alcohols such as furfuryl alcohol would be also suitable to the system. Furthermore, oxidations of aliphatic alcohols were also tested. Unfortunately, in the case of aliphatic alcohols such as dodecyl alcohol, the results were unsatisfactory even after elongating the reaction time.

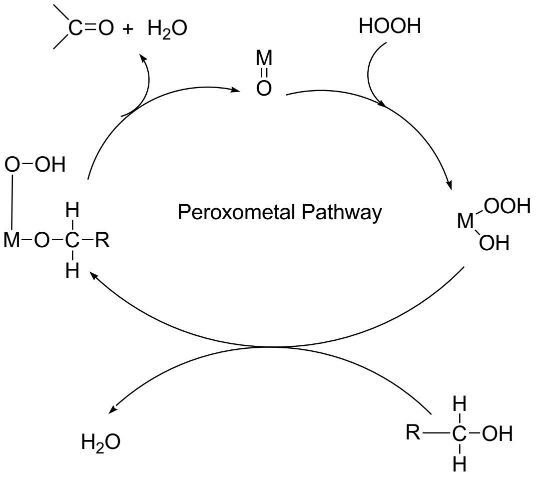
The role of polyoxometalate might act as a hydrogen acceptor during the proposed catalytic cycle. Firstly, peroxometal species are generated by hydrogen peroxide-mediated oxidation of polyoxometalate. Then, alcohol

Table 4 Oxidation of various alcohols



 6 h 100% (98%)	 6 h 99% (96%)	 5 h >99% (98%)	 8 h 98% (94%)	 5 h >99% (99%)
 8 h 96% (95%)	 8 h 95% (93%)	 10 h 90% (84%)	 10 h 84% (82%)	 16 h 81% (80%)
 14 h 83% (81%)	 16 h 86% (84%)	 12 h 90% 82%)	 20 h 70% (68%)	

Reaction conditions: alcohols (10 mmol), [PEO-didodecy limidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05 mol % of acohol), 30 % aq H_2O_2(2 equiv), rt



Scheme 2 The mechanism of oxidation of alcohols

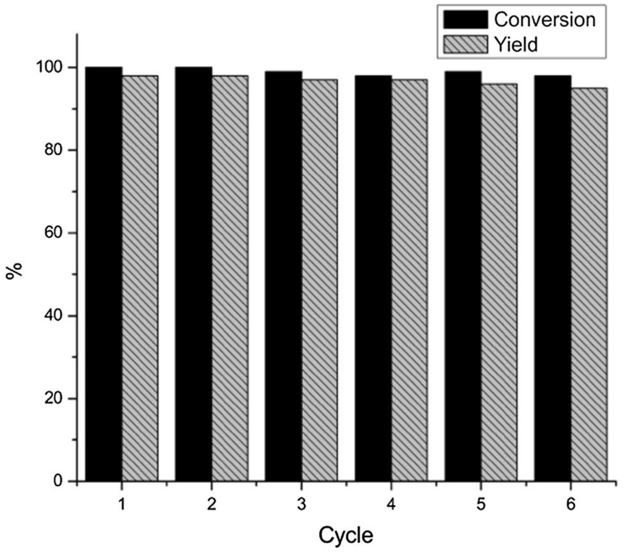


Fig. 3 Cycling reaction

coordinates to the peroxometal species to lead to alkoxy peroxometal species. The intramolecular transfer of *β*-hydrogen to peroxometal species leads to the aldehyde and polyoxometalate (Scheme 2).

The advantage of the catalytic system lies in not only the high catalytic activity with H_2O_2 as oxidant, but also the easy recovery of both catalyst and products. Since both the catalyst was immiscible with ethyl ether, the catalytic system could be recovered through extraction. The catalyst could be reused with the recharge of substrate without any treatment. The organic layer containing the products was analyzed after drying with anhydrous magnesium sulfate. When benzyl alcohol was used as a model substrate, the procedure was successfully performed for at least six times without great loss of catalytic activity (Fig. 3).

Conclusion

In conclusion, we have developed an efficient and environment-friendly method for the aerobic oxidation of alcohols with [PEO-didodecylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ as catalyst and H_2O_2 as oxidant. Owing to the exsistence of long chain, the catalyst had a good surface-active performance to promote reaction effectively. Moreover, it could be recycled and reused without significant loss of catalytic activity after six runs. For this environmentally catalyst, it would find a wider application in various reactions, which is an ongoing project.

Experimental section

All starting materials were purchased from commercial sources and used without further treatment. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. IR spectrum analysis was recorded on Nicolet IS-10 fourier transform infrared spectroscopy. High performance liquid chromatography experiments were performed on a liquid chromatograph (Shimazhu LC-20AT, Japan).

General procedure for preparation of catalyst

To a solution of PEG-1000 (0.02 mol, 20 g) in toluene (150 mL), pyridine (0.04 mol, 3.2 mL) was added, followed by the addition of thionyl chloride (0.04 mol, 2.9 mL) within 30 min under N_2 atmosphere at 0 °C. The resulting slurry was stirred for 24 h at room temperature and filtered. The toluene was then removed by rotator evaporation under reduced pressure to give intermediate **1** as a gray viscous liquid. Next, intermediate **1** (0.015 mol) was added to sodium imidazole salts solution 0.015 mol (1.25 g) which was dissolved in toluene and the mixture was stirred at 80 °C for 24 h. The reaction was determined by HPLC and evaporated under reduced pressure to give intermediate **2** as an orange liquid with a yield of 98.0 %. In the next step, intermediate **2** (0.01 mol) was added to 1-bromododecane $C_{12}H_{25}Br$ 0.02 mol (1.25 g) solution which was dissolved in toluene and the mixture was stirred at 70 °C for 20 h. The reaction was determined by HPLC and evaporated under reduced pressure to give intermediate **3** as a white viscous solid. Finally, the intermediate **3** (1.2 mmol) was mixed with $H_3[P(W_3O_{10})_4]$ 2.36 g (0.8 mmol) in dry ethanol with a mechanical stirring at 40 °C for 6 h. The obtained white solid were filtered and dried under vacuum to give the catalyst [PEO-didodecylimidazolium]$_3$[$P(W_3O_{10})_4$]$_2$ with a yield of 95.0 %.

Oxidation process of alcohols

In a typical process, benzyl alcohol (10 mmol), [PEO-dido decylimidazolium]$_3$[$PW_{12}O_{40}$]$_2$ (0.05 mol %), 30 % aq H_2O_2 (20 mmol) were then added. The mixture was stirred and under room temperature. The progress of the reaction was monitored by TLC with samples taken periodically. After completion of reaction, the mixture was extracted with ether for three times. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The product was analyzed by HPLC and purified by column chromatograph to give benaldehyde (98 % yield). The next run was performed under identical reaction conditions.

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