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Immobilized bis-layered ionic liquids/peroxotungstates as an efficient catalyst for selective oxidation of alcohols in neat water

Juan Fan, Fan Pu, Man Sun, Zhong-Wen Liu, Xiao-Yan Han, Jun-Fa Wei and Xian-Ying Shi*

An immobilized ionic liquids/peroxotungstates/SiO$_2$ catalyst was prepared and characterized. The catalyst was proved to be very efficient for the selective oxidation of primary and secondary alcohols to their corresponding carbonyls with benign H$_2$O$_2$ as an oxidant in a neat water. A 1.0 mol% (based on tungstate) dose of the catalyst was found to be sufficient for the oxidation. The catalyst is easily recovered after reaction via a simple filtration, and was reused for at least six times without a noticeable loss of the activity. Notable feature of this novel protocol is avoiding any organic co-solvent.

Introduction

The selective oxidation of alcohols to corresponding carbonyl compounds is one of the most important and fundamental transformation in organic synthesis because the carbonyl products are important intermediates for synthesizing fine chemicals, particularly medicines, flavors, fragrances, and aniline dyes.[1-5] The traditional oxidation of alcohols are carried out with stoichiometric amounts of inorganic oxidants such as Cr (VI) or Mn (VII) compounds, which generates a large amount of heavy metal waste.[6-7] From the viewpoints of green sustainable chemistry, the replacement of classic oxidants with benign counterparts is highly desirable.

As an ideal oxidant, H$_2$O$_2$ has attracted considerable attention in recent years because it is environmentally friendly, inexpensive, readily available, easy to handle, and gives water as the only byproduct.[8] Consequently, in the past decades, many catalytic procedures including homogeneous and heterogeneous systems have been developed for the selective oxidation of alcohols by using H$_2$O$_2$ as a green oxidant.[9-18] Compared with homogenous catalysts, the heterogeneous catalysts are of significantly industrial interest since they can be easily separated from the reaction mixture and recycled. Although some heterogeneous catalysts have been applied to oxidize alcohols,[19-26] many of them were carried out in toxic organic solvent such as CH$_3$CN, dioxane and ^{t}BuOH,[27-33] which can bring about environmental pollution. In a sharp contrast, the green solvents have been seen considerably less progress in the oxidation of alcohols.[34-37] Therefore, the major challenge in this area is to accomplish oxidative process in a nontoxic solvent employing an efficient solid catalyst.

Ionic liquids (ILs) with special solubility and flexible design ability of cations and anions have been employed in modifying mesoporous silica for supporting homogenous catalysts.[38-43]

Significantly, homogeneous catalytic centers can be introduced with the immobilized ILs via ion exchange and/or coordination. However, the immobilized ionic liquids reported are exclusively mono-layered ILs.[44-52] As a result, the introduced catalytic centers are very limited. To overcome this shortcoming, as given in Figure 1, we designed bis-layered ionic liquids to bind covalently to silica, which have more imidazoliums per unit area, and more counter-anions are exchangeable with anionic reactants or catalytic species.[53-56] Thus, employing this immobilized bis-layered ILs as a scaffold, other catalytic components can be introduced via ion exchange and/or coordination. Moreover, the bis-layered IL framework can offer a deeper 3D environment that closely resembles the liquid-phase character of ILs for both hydrophilic and hydrophobic reactants to move into the brushes where the active catalyst attached and for the product and by-product to move out of the catalysts. We have proved their high efficiency and recyclability for some organic reactions in neat water, such as selective oxidation of olefins or sulfoxides with H$_2$O$_2$, Suzuki and Heck coupling reaction.[53-56]

Herein, in continuation of our ongoing research on the development of novel catalytic systems for selective oxidation of organic compounds in green media, we demonstrate the application of the ILs/peroxotungstates/silica as a micro catalytic reactor for the selective oxidation of primary and secondary alcohols to their corresponding carbonyls with benign 30% H$_2$O$_2$ as an oxidant in neat water. As a result of the hydrophilic imidazoliums and hydrophobic hydrocarbon chains in the ILs, both the hydrophobic alcohols and the hydrophilic H$_2$O$_2$ oxidant can be readily diffused into the micro reactor, and give the carbonyls catalyzed by the peroxotungstates. Thus, the homogeneous reaction nature over the ILs/peroxotungstates/silica micro reactor makes the oxidation of various alcohols highly efficient, and it can

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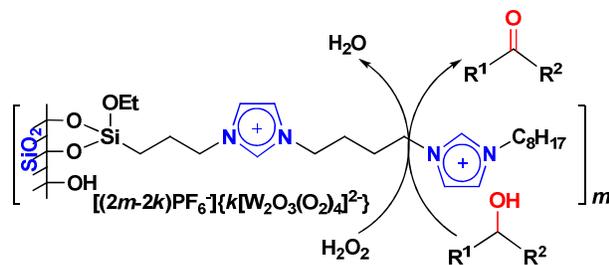
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Fig. 1 The diagram for the ILs/peroxotungstates/silica micro catalytic reactor and its possible working principle.

be easily separated from the reaction mixture. Importantly, over 95% yield was obtained for the oxidation of benzyl alcohol, and the catalyst was reused for six times without a noticeable loss of activity.

Experimental

Preparation and characterization of the catalysts

All commercial chemicals were used as received without further purification. Hydrogen peroxide (30 wt.%) was of AR grade. Before use, it was titrated using a standard $KMnO_4$ solution.

The SiO_2-BisILs[Cl] was synthesized via a 3-step route according to the procedure we previously reported[56].

The exchange between Cl^- and PF_6^- was realized by the direct reaction of the SiO_2-BiILs[Cl] and KPF_6 in CH_3CN at room temperature for 24 h. Then, it was washed consecutively with water and acetone. After drying under vacuum at 70 °C, the bis-layered ionic liquids modified SiO_2-BisILs[PF_6] was obtained.

For preparing $K_2[W_2O_3(O_2)_4]$, 10 mL 30% H_2O_2 was added under stirring to the solution of $K_2WO_4 \cdot 2H_2O$ (0.725, 2 mmol) in 10 mL water at room temperature. Then, diluted HCl aqueous solution was added until the solution was changed from yellow to colorless, indicating the formation of $K_2[W_2O_3(O_2)_4]$. After this, 1 g of the SiO_2-BisILs[PF_6] was added to the colorless solution for the anion exchange. After stirring at room temperature for 36 h, it was filtrated and dried. Finally, the SiO_2-BisILs[$W_2O_3(O_2)_4$] catalyst was obtained.

The porous properties of the catalyst were evaluated by the nitrogen adsorption/desorption method at -190 °C on a Peking Pioneer-2002 ST-03A instrument. The surface area of the catalyst was determined by using the Brunauer–Emmett–Teller (BET) method, and Pore size distributions were calculated from the desorption branch using the BJH model. The SEM-EDAX was performed on a Philips-FEI Quanta 200 scanning electron microscopy equipped with an EDAX energy dispersive X-ray analysis. The elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded on a Bruker Equinox-55 spectrophotometer (KBr pellets in the range of 400–4000cm^{-1}). The thermogravimetric differential scanning calorimetry (TG-DSC) was carried out on a Q1000DSC+LNCS+FACSQ600SDT thermogravimetric analyzer. The sample was heated under air atmosphere from room temperature to 800 °C at a ramp of 10 °C/min.

Typical procedure for the selective oxidation of alcohols to carbonyl compounds

In a typical experimental procedure, to a 10mL flask, alcohol (1 mmol) and 30 wt.% H_2O_2 (1.4 mmol), the catalyst (1.0 mol% with respect to the alcohol) and 2mL deionized water were added successively. The resulting mixture was stirred electromagnetically at 90 °C and monitored using TLC. After the completion of the reaction, the catalyst was separated by filtration under reduced pressure, was washed with EtOH (3 × 5mL) and dried in vacuum. The excess hydrogen peroxide was destroyed using MnO_2. The filtrate was concentrated under reduced pressure. Determination of products in the reaction mixture was performed on a QP2010UItra GC-MS instrument (EI) with HP-5 columns. Quantitative analyses of the reaction products were performed with an Agilent 6890 N using a capillary column (HP-5, 30m × 0.25mm × 0.53 μm) with an FID detector.

Results and discussion

Characteristics of the catalyst

Following the preparation procedure, the formation of the SiO_2-BisILs[$W_2O_3(O_2)_4$] catalyst was schematically shown in Scheme 1. From IR results (Fig. S1 in Supporting information), the v(C–H) at 3163, 2943, 2858cm^{-1} and v(C–N) at 1639 cm^{-1}clearly confirms the attachment of the ILs onto silica, leading to the formation of SiO_2-BisILs[Cl]. Moreover, 19.57, 2.88, and 7.39 wt.% for C, H, and N, respectively, were determined by elemental analyses. From the TG results (Fig. S2 in Supporting information), the amount of the BisILs[Cl] was determined to be about 28.72 wt.%. Moreover, the different slopes of the TG curves suggest that the ILs may be immobilized on silica via a covalent bond as shown in Scheme 1.

After anion exchanging between Cl^- and PF_6^-, a weight loss of 32.31 wt.% was obtained from the TG analysis (Fig. S2 in Supporting information), which matches well with the substitute of
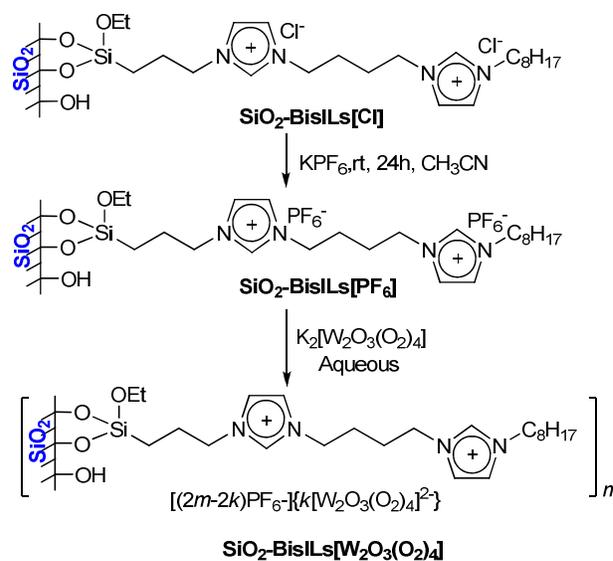
Scheme 1 Preparation of ILs/peroxotungstates/silica catalyst.

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PF_6^- for Cl^-. This was also confirmed from the SEM-EDAX results (Fig. S3 in Supporting information). Moreover, the absence of chloride from the EDAX analyses reveals that the anion exchange between Cl^- and PF_6^- is completely finished under the conditions applied, leading to the formation of SiO_2-BisILs[PF_6].

The further formation of SiO_2-BisILs[$W_2O_3(O_2)_4$] was apparently seen from the TG results (Fig. S2 in Supporting information), in which its weight loss of 24.64 wt.% is clearly smaller than that of SiO_2-BisILs[Cl] (28.72 wt.%). Moreover, the IR spectrum (Fig. S1 in Supporting information) shows the characteristic peaks of $[W_2O_3(O_2)_4]^{2-}$ structure at 947cm^{-1} for v(W=O), 839cm^{-1} for v(O–O), and 563 cm^{-1} for v_{asym}(WO_2), which is similar to the previous report.[58] The EDAX results (Fig. S4 in Supporting information) conclusively indicate the successful introduction of peroxotungstates. However, the presence P and F indicates that the anion exchange between $[W_2O_3(O_2)_4]^{2-}$ and PF_6^- is not complete. Based on these results, the amount of the tungsten and phosphorus are estimated to be 0.334 and 0.165 mmol/g, respectively, revealing that the catalyst contains about 0.25 mmol of imidazolium/g.

The porous properties of the SiO_2-BisILs[$W_2O_3(O_2)_4$] are important for its catalytic functions as a result of the liquid-phase reaction. From the N_2 adsorption-desorption isotherms of the catalyst (Fig. 3, **a**), a type IV isotherm together with an H4-type hysteresis loop was observed according to the IUPAC classification.[57] The BET surface of the catalyst was determined to be 136.8 m^2/g. The parallel part of the hysteresis loop in the regions of $P/P_0 > 0.7$ implies open and cylindrical pores. A peak pore size of about 8.06 nm was determined from the pore size distribution calculated by the BJH method (Fig. 3, **b**). Moreover, the mesoporous structure of the catalyst was clearly reflected from the sharp pore size distribution. Thus, high catalytic performance of SiO_2-BisILs[$W_2O_3(O_2)_4$] for the titled reaction can be reasonably expected from its mesoporous structure with an average pore size of about 8 nm, very narrowed pore size distribution, and a reasonably high surface area.
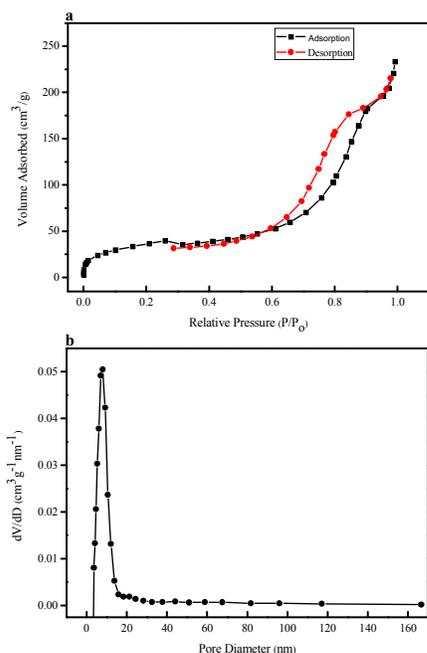
Optimizing reaction conditions

In the absence of the catalyst, control experiment indicates that the oxidation of benzyl alcohol under the conditions of H_2O_2/alcohol molar ratio of 1.4, temperature of 90 ^{o}C and reaction time of 18 h affords a negligible amount of benzaldehyde (Table 1, entry 1). When either SiO_2-IL[Cl] or SiO_2-IL[PF_6] were used, the yields of benzaldehyde were less than 20% (Table 1, entries 3, 4). By using $K_2[W_2O_3(O_2)_4]$ as a homogeneous catalyst, a 76% yield of benzaldehyde was obtained under the same conditions. These results clearly indicate that the peroxotungstates is the effective catalytic site for the selective oxidation reactions. Under the same conditions, a very high yield of 96% was achieved by using SiO_2-BisILs[$W_2O_3(O_2)_4$] as a catalyst. Thus, the hydrophobic and hydrophilic environment makes the SiO_2-BisILs[$W_2O_3(O_2)_4$] an efficient micro catalytic reactor for the selective oxidation of hydrophobic benzyl alcohol with hydrophilic H_2O_2. Since the anion exchange between $[W_2O_3(O_2)_4]^{2-}$ and PF_6^- is more efficient than that between $[W_2O_3(O_2)_4]^{2-}$ and Cl^-, the catalyst prepared by direct exchanging Cl^- with peroxotungstates also gave a lower yield of product (Table 1, entry 5), which can be reasonably ascribed to the lower loading of peroxotungstates.

The oxidation of alcohols to carbonyls was studied in detail by optimizing the reaction variables such as the molar ratio of alcohol/H_2O_2, alcohol/catalyst, and reaction temperature. Benzyl alcohol was selected as a model substrate to optimize reaction conditions and water was used as a solvent. In view that the choice of reaction temperature is vital to the oxidation reaction, the influence of the reaction temperature on the selective oxidation of benzyl alcohol was firstly optimized under the conditions of 1 mol% catalyst, H_2O_2/alcohol molar ratio of 1.4, and reaction time of 18 h. With increasing the reaction temperature from 60 to 95°C, the yield of benzaldehyde was firstly increased almost linearly, and the highest yield of 96% was obtained at 90°C (Fig. 3). The further increasing of the reaction performed to 95 ^{o}C afforded a sharp

Fig. 2 Nitrogen adsorption-desorption isotherm (a) and the BJH pore size distribution of the SiO_2-BisILs[$W_2O_3(O_2)_4$] (b).

Table 1 Selective oxidation of benzyl alcohol to benzaldehyde employing different catalysts[a]
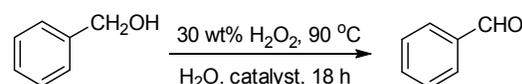
Entry	Catalyst	Yield(%)[b]
1	No	trace
2	SiO_2-BisILs[$W_2O_3(O_2)_4$]	96
3[c]	SiO_2-BisILs[Cl]	13
4[d]	SiO_2-BisILs[PF_6^-]	16
5[e]	SiO_2-BisILs[$(2m-2k)Cl^-$]{$k[W_2O_3(O_2)_4]^{2-}$}	33
6	$K_2[W_2O_3(O_2)_4]$	76

[a] Condition: alcohols (1 mmol), H_2O_2 (1.4 mmol), H_2O (2 mL), catalyst (1mol%, based on the content of tungsten), were stirred at 90℃ for 18 h. [b] GC yields. [c]SiO_2-BisILs[Cl] as catalyst. [d] SiO_2-BisILs[PF_6^-] as catalyst. [e]Catalyst prepared by the chloride anions directly exchanged with peroxotungstates.

decrease of the yield due to the formation of over-oxidation products. Thus, the optimal temperature of 90 °C was recommended.

To continue with the study of the reaction optimization, the effect of amount of catalyst on the yield was studied by using 1.4 equiv. H_2O_2 at 90 °C for 18 h, and the results are given in Fig. 4. Noticeably, only 1 mol% catalyst is sufficient for this transformation. However, when the amount of the catalyst was further increased from 1 to 2 mol%, the yield of benzaldehyde was continuously decreased, which can be reasonably ascribed as the over-oxidation of the benzaldehyde as confirmed from GC analysis results.

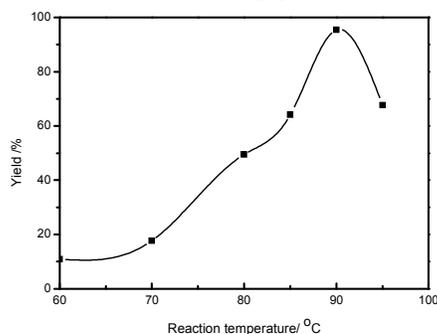The influence of the amount of H_2O_2 was also investigated with

Fig. 3 Effect of reaction temperature on the selective oxidation of benzyl alcohol to benzylaldehyde.
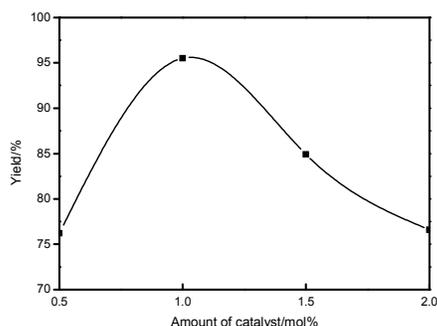

Fig. 4 Effect of the amount of catalyst on the selective oxidation of benzyl alcohol to benzylaldehyde.
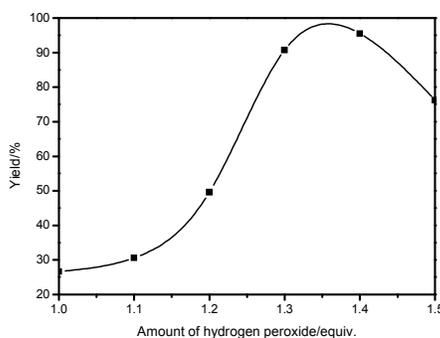

Fig. 5 Effect of the amount of hydrogen peroxide on the selective oxidation of benzyl alcohol to benzylaldehyde.

1 mol% catalyst at 90 °C for 18 h (Fig. 5). The highest yield of the product was obtained at 1.4 equiv. H_2O_2, which is slightly higher than the stoichiometric value. The reason may be that the decomposition of some H_2O_2 occurs in the oxidation process and the excess of oxidant could increase the reaction rate.

The generality of the catalytic system

With the optimized conditions in hand, a variety of alcohols including aromatic and aliphatic alcohols were employed to investigate the generality of this oxidative system with neat water as a solvent. From the results given in Table 2, although substituted-benzylic alcohols were readily selectively oxidized to the desired products in satisfied yields, a significant electronic effect of substituted groups on the activity was observed. The electron-rich benzylic alcohols such as methyl and methoxy, in generally, gave better yields (Table 2, entries 2, 3). Benzylic alcohols bearing weak electron-withdrawing halogen substituents led to a decreased efficiency (Table 2, entries 4-6), which may due to the formation ofthe acid as a by-product. The presence of a strong electron withdrawing group of NO_2 in the phenyl ring afforded the desired product in a lower yield of 75% (Table 2, entry 7). Moreover, the steric effect could be observed by comparing the results with 2-bromobenzylic alcohol and 4-bromobenzylic alcohol as a substrate (Table 2, entries 5, 6). Although this oxidation tolerated dual-substituted benzylic alcohol, the lowest yield of 67% was achieved with 3,4-dimethoxylbenzylic alcohol (Table 2, entry 8).

Apart from aromatic primary alcohols, aliphatic primary alcohol is also active in this transformation, and provides the aldehyde in an excellent yield (Table 2, entry 9). Moreover, aromatic secondary

Table 2 The selective oxidation of different alcohols catalyzed by SiO_2-BisILs$[W_2O_3(O_2)_4]$ with H_2O_2[a]

Entry	R^1	R^2	Time (h)	Selectivity[b] (%)	Yield[c] (%)
1	C_6H_5	H	18	98	96
2	$4\text{-}CH_3OC_6H_4$	H	18	95	94
3	$2\text{-}CH_3C_6H_4$	H	18	96	88
4	$4\text{-}ClC_6H_4$	H	22	87	81
5	$4\text{-}BrC_6H_4$	H	22	85	80
6	$2\text{-}BrC_6H_4$	H	22	88	73
7	$4\text{-}NO_2C_6H_4$	H	30	82	75
8	$3,4\text{-}(CH_3O)_2C_6H_3$	H	26	97	67
9	cyclohexyl	H	24	93	90
10	n-hexyl	CH_3	26	99	91
11	C_6H_5	C_6H_5	24	100	58
12	C_6H_5	CH_3	18	99	88
13	$R^1=R^2=(CH_2)_5$		26	98	84
14	C_6H_5	H	18	99	89

[a] Conditions: alcohols (1 mmol), H_2O_2 (1.4mmol), H_2O (2 mL), catalyst (1 mol%) based on content of tungstate, were stirred at 90℃.[b]Select.=selectivity. The selectivity of product was calculatedbasedon GC.[c]GC yields.

alcohols and aliphatic alcohols could also be applied in this oxidation system and provided ketones in good yields (Table 2, entries 10-13).

To gain an insight into the applicability of this catalytic system, the scaled-up experiment was carried out employing benzyl alcohol as a substrate under the optimized conditions. When the amount of benzyl alcohol increases from 1to 5 mmol, only a limited decrease in the yield of benzaldehyde was observed(Table 2, entry 14), which demonstrates that this heterogeneous oxidation has a potentially scaled-up application.

The recycling of SiO$_2$-BisILs[W$_2$O$_3$(O$_2$)$_4$]

One of the main advantages of heterogeneous catalysts is the convenience of separation and the successive catalytic cycles. The recyclability of the developed SiO$_2$-BisILs[W$_2$O$_3$(O$_2$)$_4$] was evaluated by performing consecutive cycles of the oxidation of benzyl alcohol under the optimized conditions. After aprevious catalytic run, the catalyst was separated from the reaction solution, washed several times with ethanol to remove any physically absorbed molecules, dried and then reused in the next catalytic run. As shown in Fig. 6, after 6 cycles, a steady yield of above 90% was still kept, indicating that the activity of the catalyst did not change significantly compared with the fresh sample. This is clearly supported by the IR results (Fig. S5 in Supporting information), in which similar IR patterns are obtained for the fresh and the recovered catalyst after used for six times. Moreover, the BET surface area (130 m^2/g) and the amount of the tungsten (0.328 mmol/g) over the catalyst used for 6 times were near identical to those of the fresh catalyst, i.e., 117 m^2/g and 0.334 mmol/g. Thus, the developed catalyst is very stable under the oxidation conditions.

Conclusions

The SiO$_2$-BisILs[W$_2$O$_3$(O$_2$)$_4$] as a micro catalytic reactor, which combines the advantages of an ionic liquids and peroxotungstates, has been successfully applied for the selective oxidation of primary and secondary alcohols to corresponding carbonyl compounds with benign H$_2$O$_2$ as an oxidant in neat water. It avoids the use of any organic co-solvent, and high yields of carbonyl compounds
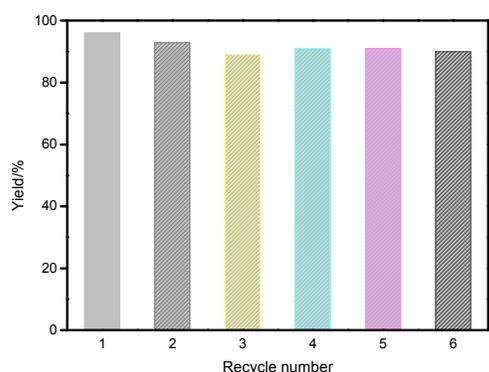
any organic co-solvent, and high yields of carbonyl compounds were achieved. The catalyst can be easily recovered and reused at least for six times without significant loss of activity. Because of its easy recyclability, the use of hydrogen peroxide as an oxidant, and neat water as a medium, it distinguishes itself by green and economical advantages from other supported catalysts.

Acknowledgements

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Fig. 6 Reusability studies of catalyst (1 mmol alcohols, 1.4 mmol H$_2$O$_2$, 2 mL H$_2$O, 1mol% catalyst based on content of tungstate, were stirred at 90℃, GC yields).

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Graphical Abstract

Immobilized bis-layered ionic liquids/peroxotungstates as an efficient catalyst for selective oxidation of alcohols in neat water

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An environmentally benign and reusable immobilized bifunctional ionic liquid/peroxotungstate catalyst has been developed for the selective oxidation of alcohols to corresponding carbonyls with aqueous H_2O_2 in neat water without any co-organic solvent. The catalyst can be reused at least six times without noticeable loss of the catalytic activity.