Peroxotungstates immobilized on multilayer ionic liquid brushes-modified silica as an efficient and reusable catalyst for selective oxidation of sulfides with H_2O_2

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ABSTRACT

Peroxotungstates held in a series of different supported ionic liquid brush catalysts were synthesized and characterized. Their catalytic performance towards the selective oxidation of sulfides with aqueous hydrogen peroxide was investigated under mild conditions. We found that the catalytic activities of the different catalysts depend on the number of supported ionic liquid layers and N-end-capped alkyl group on the imidazole ring. The highest yield of methyl phenyl sulfoxide was obtained using the BisILs-C_8H_{17}-W2 catalyst under optimum conditions. The sulfides were selectively oxidized to sulfoxides in high yields with trace sulfones detected by GC upon using 1.1 equivalents of H_2O_2. At 2.5 equivalents of H_2O_2 the sulfones were found to be the main products. It is noteworthy that the catalyst resulted in high chemoselectivity towards sulfur groups with unsaturated double bonds even though excess hydrogen peroxide was used in addition to exhibiting high catalytic activity. There was no apparent loss of catalytic efficiency until the 8th cycle.

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1. Introduction

The increasing amount of interest directed towards sulfoxides and sulfones has stimulated research on their efficient synthesis because of their extensive applications as synthetic intermediates for the construction of various chemically and biologically active molecules [1,2]. The selective oxidation of sulfides is a simple technique that can be used to obtain sulfoxides and sulfones. Many reagents are available for the oxidation of sulfides such as halogen compounds [3–6], nitrates [7], transition metal oxides [8], oxygen and hydrogen peroxide [9–17]. Among them, hydrogen peroxide has attracted much attention over the years because it forms harmless by-products and product work-up is simple [18–21].

Previous research has shown that soluble transition metal based complexes are effective catalysts for the oxidation of sulfides when using hydrogen peroxide as an oxidant [22–26]. Although homogenous catalysts have favorable catalytic abilities [27,28], heterogeneous catalysts are of significant industrial interest as they can be easily separated from the reaction mixture and recycled. Some heterogeneous catalysts have been applied to the oxidation

of sulfides [29–33]. However, these catalytic systems suffer from at least one of the following shortcomings: long reaction time, low conversion of sulfide, bad selectivity between sulfoxide and sulfone, high catalyst quantities and excessive H_2O_2.

In our previous work, we found that the catalysts of peroxotungstates that were immobilized on mono-layered ionic liquid-modified silica worked well for the oxidation of sulfides [34]. However, the narrow imidazoliums on the carrier limited the amount of catalytic active centers because only one imidazolium was present on each of the side chains. Recently, we reported that a series of supported multilayered ionic liquids, which have more imidazoliums on each of the side chains (referred to as "ionic liquid brushes") because of their brush-like features were useful as efficient and multifunctional catalysts for the Suzuki reaction [35]. These coral-like brushes provide an ionic liquid micro-environment for substrates, reactants and active species, and have the advantage of ease separation by simple filtration. The recovery and recycling of these brushes provides environmental benefits and economical viability. As a part of our ongoing research about the use of ionic liquid brushes as promoters for organic reactions, peroxotungstates that are held in ionic liquid brushes (Fig. 1) were prepared and their catalytic properties were determined during the oxidation of sulfides under mild conditions because a variety of tungsten-based homogeneous catalysts are known to have high activities in useful oxidation procedures when using hydrogen peroxide as an oxidant.

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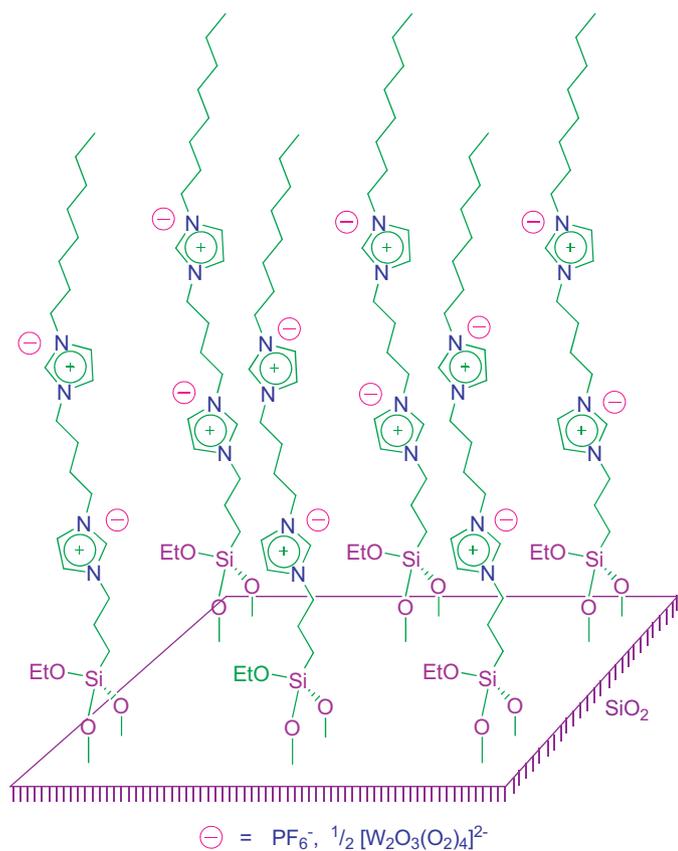
Fig. 1. Silica immobilized peroxotungstates ionic liquids brushes.

2. Experimental

2.1. Materials and apparatus

Unless otherwise stated, all reagents were purchased from commercial sources and used without purification. Flash chromatography was performed with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. The SEM-EDAX was performed on a Philips-FEI Quanta 200 scanning electron microscopy equipped with an EDAX energy dispersive X-ray analysis. The BET surface areas of materials were measured by nitrogen adsorption Peking Pioneer-2002 ST-03A. C, H and N element analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded separately on a Bruker Equinox-55 spectrophotometer (KBr pellets in the range 400–4000 cm^{-1}). ICP-MS was measured by X series Π mass spectrometer. ^{1}H NMR and ^{13}C MNR spectra were recorded on a Bruker AVANCE300 MHz spectrometer (TMS as an internal standard). GC analysis was performed on an Agilent 6890N using a capillary column (HP-5 30 m × 0.25 mm × 0.53 μm) with a FIT detector.

2.2. Preparation of catalysts

2.2.1. Preparation of SiO$_2$-BisILs-R

SiO$_2$-1 and SiO$_2$-2 were synthesized according to previous report [34,35]. The mixture of 2.0 g SiO$_2$-2 and 0.034 mol alkyl halide was vigorously stirred in refined toluene under refluxed condition for 24 h. After filtered, the resulting materials were washed by Soxhlet extraction with ethanol as solvent. The ionic liquid modified silica SiO$_2$-BisILs-R was prepared by the direct reaction of the above precursor and KPF$_6$ in CH$_3$CN at room temperature for 24 h.

After the reaction, the obtained materials were washed consecutively with water and acetone, then, dried under vacuum at 70 °C over night.

SiO$_2$-BisILs-CH$_3$ (R = CH$_3^-$): Elemental analysis: C, 12.35%; H, 2.38%; N, 2.01%. IR (KBr disk): 3050, 2937, 2866 cm^{-1}, ν(C–H); 1642 cm^{-1}, ν(C=N); 833 cm^{-1}, ν(PF$_6^-$). BET surface areas: 107 m^2/g.

SiO$_2$-BisILs-C$_4$H$_9$ (R = n-C$_4$H$_9^-$): Elemental analysis: C, 17.03%; H, 2.09%; N, 2.69%. IR (KBr disk): 3055, 2942, 2882 cm^{-1}, ν(C–H); 1627 cm^{-1}, ν(C=N); 822 cm^{-1}, ν(PF$_6^-$). BET surface areas: 67 m^2/g.

SiO$_2$-BisILs-C$_8$H$_{17}$ (R = n-C$_8$H$_{17}^-$): Elemental analysis: C, 12.48%; H, 1.80%; N, 2.96%. IR (KBr disk): 3162, 2938, 2860 cm^{-1}, ν(C–H); 1636 cm^{-1}, ν(C=N); 832, ν(PF$_6^-$). BET surface areas: 117 m^2/g.

SiO$_2$-BisILs-C$_{12}$H$_{25}$ (R = n-C$_{12}$H$_{25}^-$): Elemental analysis: C, 13.22%; H, 1.96%; N, 2.34%. IR (KBr disk): 3061, 2939, 2867 cm^{-1}, ν(C–H); 1639 cm^{-1}, ν(C=N); 830 cm^{-1}, ν(PF$_6^-$). BET surface areas: 82 m^2/g.

SiO$_2$-BisILs-C$_6$H$_5$CH$_2$ (R = C$_6$H$_5$CH$_2^-$): Elemental analysis: C, 14.22; H, 1.68; N 3.01%. IR (KBr disk): 3053, 2928, 2882 cm^{-1}, ν(C–H); 1641 cm^{-1}, ν(C=N); 828 cm^{-1}, ν(PF$_6^-$). BET surface areas: 34 m^2/g.

2.2.2. Preparation of BisILs-R-W2 catalysts

10 ml 30% H$_2$O$_2$ was added to the solution of K$_2$WO$_4$·2H$_2$O (0.725, 2 mmol) in 10 ml water while being stirred at room temperature [36,37], the resulting yellow solution was treated with dilute HCl until it just turned colorless. 1 g of the SiO$_2$-BisILs-R was added to this colorless solution and the suspension was stirred at room temperature for 24 h. During the reaction, binuclear peroxotungstate anions were exchanged on the ionic liquid-modified silica SiO$_2$-BisILs-R. After filtration and dry, the bis-layered ionic liquid modified SiO$_2$ catalysts were obtained.

BisILs-CH$_3$-W2 (R = CH$_3^-$): Elemental analysis: C, 11.88; H, 1.93; N, 1.98%. IR (KBr disk): 3162, 2940, 2866 cm^{-1}, ν(C–H); 1641 cm^{-1}, ν(C=N); 833 cm^{-1}, ν(PF$_6^-$); 934 cm^{-1}, ν(W=O); 843 cm^{-1}, ν(O–O); 727 cm^{-1}, ν(W$_2$O); 559 cm^{-1}, ν(W(O$_2$)). BET surface areas: 71 m^2/g. The loading amount of tungsten and phosphorus are 0.332 and 0.103 mmol/g respectively.

BisILs-C$_4$H$_9$-W2 (R = n-C$_4$H$_9^-$): Elemental analysis: C, 15.62; H, 1.93; N, 2.38%. IR (KBr disk): 3079, 2942 cm^{-1}, ν(C–H); 1625 cm^{-1}, ν(C=N); 821 cm^{-1}, ν(PF$_6^-$); 932 cm^{-1}, ν(W=O); 844 cm^{-1}, ν(O–O); 686 cm^{-1}, ν(W$_2$O); 559 cm^{-1}, ν(W(O$_2$)). BET surface area: 68 m^2/g. The loading amount of tungsten and phosphorus are 0.326 and 0.559 mmol/g respectively.

BisILs-C$_8$H$_{17}$-W2 (R = n-C$_8$H$_{17}^-$): Elemental analysis: C, 12.06; H, 1.71; N, 2.64%. IR (KBr disk): 3166, 2937, 2864 cm^{-1}, ν(C–H); 1638 cm^{-1}, ν(C=N); 831 cm^{-1}, ν(PF$_6^-$); 935 cm^{-1}, ν(W=O); 844 cm^{-1}, ν(O–O); 731 cm^{-1}, ν(W$_2$O); 560 cm^{-1}, ν(W(O$_2$)). BET surface area: 103 m^2/g. The loading amount of tungsten and phosphorus are 0.334 and 0.165 mmol/g respectively.

BisILs-C$_{12}$H$_{25}$-W2 (R = n-C$_{12}$H$_{25}^-$): Elemental analysis: C, 11.99; H, 1.72; N, 1.82%. IR (KBr disk): 3057, 2931 cm^{-1}, ν(C–H); 1642 cm^{-1}, ν(C=N); 828 cm^{-1}, ν(PF$_6^-$); 942 cm^{-1}, ν(W=O); 875 cm^{-1}, ν(O–O); 685 cm^{-1}, ν(W$_2$O); 560 cm^{-1}, ν(W(O$_2$)). BET surface areas: 65 m^2/g. The loading amount of tungsten and phosphorus are 0.312 and 0.51 mmol/g respectively.

BisILs-C$_6$H$_5$CH$_2$-W2 (R = C$_6$H$_5$CH$_2^-$): Elemental analysis: C, 13.27; H, 1.58; N, 2.63%. IR (KBr disk): 3072, 2932 cm^{-1}, ν(C–H); 1636 cm^{-1}, ν(C=N); 830 cm^{-1}, ν(PF$_6^-$); 928 cm^{-1}, ν(W=O); 882 cm^{-1}, ν(O–O); 726 cm^{-1}, ν(W$_2$O); 564 cm^{-1}, ν(W(O$_2$)). BET surface area: 20 m^2/g. The loading amount of tungsten and phosphorus are 0.326 and 0.284 mmol/g respectively.
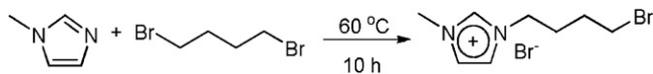
Scheme 1. Synthesis of 1-(4-bromobutyl)-3-methylimidazolium bromide.

2.2.3. Preparation of SiO$_2$-TriILs-CH$_3$

The mixture of 1-methylimidazole (3.52 g, 43 mmol) and 1,4-dibromobutane (20 ml) was heated to 60 °C under strongly stirring for 10 h. Then the mixture was cooled to room temperature and extracted by deionized water. After the removal of residual, a yellow viscous liquid 1-(4-bromobutyl)-3-methylimidazolium bromide was obtained in 84% yield (Scheme 1). Anal. Calc. for C$_8$H$_{14}$Br$_2$N$_2$: C, 32.23%; H, 4.70%; N, 9.40%; Found: C, 32.10%; H, 4.75%; N, 9.43%.

The suspension of SiO$_2$-2 (2.45 g) and 1-(4-bromobutyl)-3-methylimidazolium bromide (0.90 g, 3.02 mmol) in DMF (20 ml) was stirred at 90 °C for 24 h. After filtered and washed with ethano, the powder was extracted by Soxhlet Extractor with ethanol as solvent and dried overnight. The SiO$_2$-TriILs-CH$_3$ was prepared by the direct reaction of the above precursor and KPF$_6$ in CH$_3$CN at room temperature for 24 h. After the completion of reaction, the obtained material was washed consecutively with water and acetone, then, dried under vacuum at 70 °C over night. Elemental analysis: C, 12.10%; H, 1.93%; N, 3.19%. IR (KBr disk): 3084, 2925, 2851 cm^{-1}, ν(C–H); 1568 cm^{-1}, ν(C=N); 826 cm^{-1}, ν(PF$_6^-$). BET surface areas: 229 m^2/g.

2.2.4. Preparation of TriILs-CH$_3$-W2 catalyst

The preparation of SiO$_2$-TriILs-CH$_3$-W2 catalyst was similar to that of BisILs-CH$_3$-W2. Elemental analysis: C, 11.23; H, 1.82; N, 2.87%. IR (KBr disk): 2925, 2843 cm^{-1}, ν(C–H); 1655 cm^{-1}, ν(C=N); 835 cm^{-1}, ν(PF$_6^-$); 951 cm^{-1}, ν(W=O); 882 cm^{-1}, ν(O–O); 698 cm^{-1}, ν(W$_2$O); 557 cm^{-1}, ν(WO$_2$). BET surface area: 211 m^2/g. The loading amount of tungsten and phosphorus are 0.506 and 0.607 mmol/g respectively.

2.3. Catalytic reactions

2.3.1. The typical procedure for the selective oxidation of sulfides to sulfoxides

To a 25 ml flask with a mixed solvent of MeOH/CH$_2$Cl$_2$ (1:1 volume ratio), the catalyst (1.5 mol% with respect to substrate), sulfide (1 mmol) and 30% aqueous hydrogen peroxide (1.1 mmol) were added successively. The resulting mixture was stirred electromagnetically at room temperature. The reaction was monitored by TLC. After the completion of the reaction, the catalysts were separated by filtration, washed with EtOAc (3 × 5 ml), and dried in vacuum. The combined organic layer was dried with anhydrous MgSO$_4$, and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography using petroleum ether-EtOAc as eluent.

2.3.2. The typical procedure for the selective oxidation of sulfides to sulfones

The methods of oxidizing sulfides to sulfones were similar to that of sulfoxides except that the ratio of catalyst, H$_2$O$_2$, and sulfide was changed from 1.5:110:100 to 2:250:100.

3. Results and discussion

3.1. Catalysts preparation

The peroxotungstates in the ionic liquid brushes (Scheme 2) were prepared by ion-exchange between the immobilized ionic liquid brushes and aqueous K$_2$[W$_2$O$_3$(O$_2$)$_4$], as shown in Scheme 2. The results of elemental analysis, IR spectra and SEM–EDAX studies of the catalysts showed that the ionic liquid anion PF$_6^-$ was not exchanged completely by the binuclear peroxotungstate anion. Therefore, the characteristic homogeneous reaction of the ionic liquid changed to that of a heterogeneous catalyst. Additionally, the grafted ionic liquid avoids the increase in cost associated with some loss in the homogeneous system.

3.2. Characterization of the intermediates and catalysts

The elemental analysis, BET surface areas, and metal loading of intermediates and catalysts are summarized in Table 1. Elemental analysis revealed that the amount of nitrogen in three intermediates was different (entries 2, 5 and 7). The nitrogen atom content in the multilayered ionic liquids were higher than that in the monolayer ionic liquid, which shows that there are more imidazolium ions in the multilayered ionic liquids. Accordingly, they could provide more abundant reaction environment of ionic liquid. Compared with the amount of tungsten loaded onto the catalysts (entries 3, 6, and 8), the amounts of tungsten loaded onto the surface of the multilayered ionic liquids were obviously higher than that of the monolayer ionic liquid. Compared with the initial intermediate SiO$_2$-1, the BET surface areas of the other intermediates and the final catalysts decreased significantly. This is consistent with the decrease in BET surface area of the carrier upon subsequent modification by organic groups.

### 3.3. The catalytic abilities of different supported catalysts

3.3.1. The influence of the number of layers of ionic liquid on the catalytic ability

The catalytic abilities of the different catalysts were investigated using methyl phenyl sulfide as a model substrate under the same reaction conditions. The results are listed in Table 2 and show that although the sulfoxides could be obtained in high yields using 30% hydrogen peroxide upon catalysis by various catalysts, the catalytic activities of these catalysts greatly depend on the number of loaded ionic liquid layers and the end-capped groups. As expected, the multilayer catalysts performed better than the monolayer cat-

Table 1
Analytical data of intermediates and catalysts.

Entry	Compound	Elemental analysis (%)			BET SA (m^2 g^{-1})	Metal loading (mmol/g)
		C	H	N		
1[a]	SiO$_2$-1	6.46	1.09		325	
2[a]	SiO$_2$-2-Im (mono)	6.03	0.89	1.65	300	
3[a]	Mono-W2-Im	5.08	0.74	1.35	199	0.22
4	SiO$_2$-2	19.57	2.88	7.39	285	
5	SiO$_2$-BisILs-CH$_3$	12.35	2.38	2.01	107	
6	BisILs-CH$_3$-W2	11.88	1.93	1.98	71	0.332
7	SiO2-TriILs-CH$_3$	12.10	1.93	3.19	229	
8	TriILs-CH$_3$-W2	11.23	1.82	2.87	211	0.506

[a] The intermediates and catalyst are reported in literature [34].

Scheme 2. Preparation of silica-immobilized ionic liquid brush catalysts.
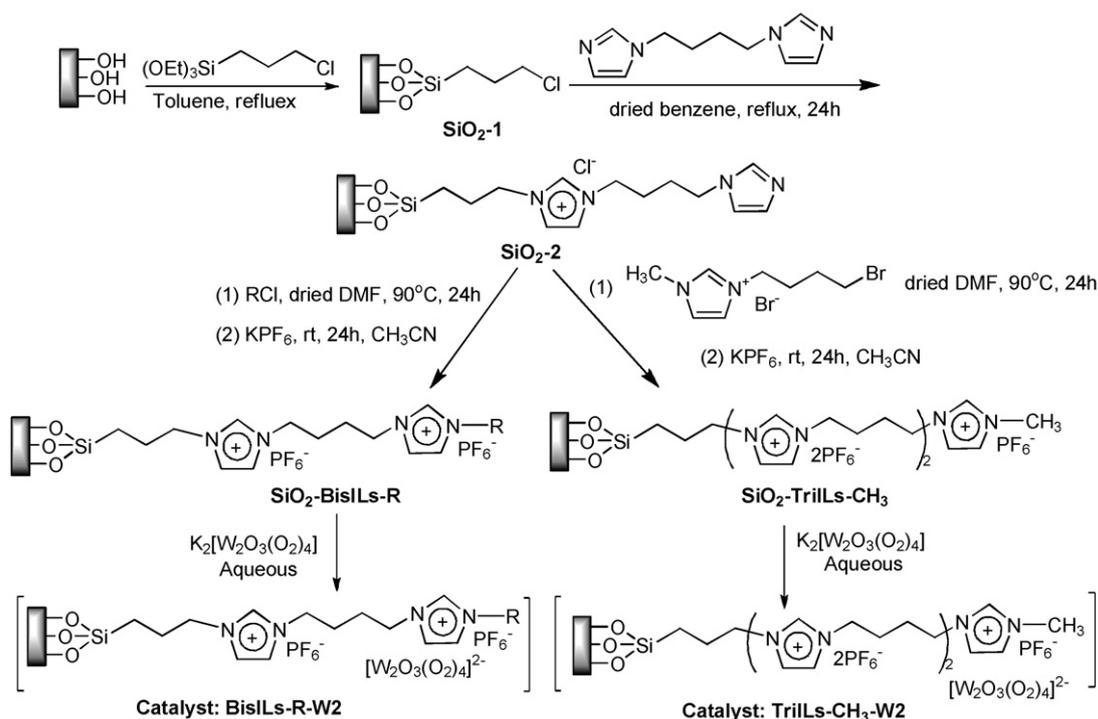
alyst (entry entries 1, 2, 7). For instance, in the reaction where a 91.9% yield of phenyl methyl sulfoxide was obtained when using the monolayer ionic liquid modified catalyst, 2.5 h (entry 1) was required. By comparison, a yield of up to 91% was obtained after only 1.5 h when using the multilayer ionic liquid catalysts (entries 2, 7).

The reason for this may be that compared with the monolayer ionic liquid catalyst, the multilayer ionic liquid catalysts have more prominent three-dimensional environment characteristics, which closely resembles the liquid phase character of ionic liquids and thus eases the approach of substrates or reagents to the catalytic species.

Additionally, the multilayer ionic liquid catalysts show good flexibility because of the larger amount of imidazoliums on each of the side chains. These properties give them better mobility, hydrophobicity and homogeneity, which provide a good environment for the reaction. However, the catalytic activity of the trilayer analogue was unexpectedly lower than that of the dilayer analogues (entry 2 vs 7). This may be because the imidazolium ions and the near the surface of the silica could not play their rules completely in the catalytic reaction since the reactants might access the deeper layer with difficulty.

Table 2
The catalytic abilities of different catalysts in oxidation of methyl phenyl sulfoxides.[a]

Entry	Catalyst	Time (h)	Yield (%)[b]
1[c]	Mono-W2-Im	2.5	91.9
2	BisILs-CH$_3$-W2	1.5	93.4
3	BisILs-C$_4$H$_9$-W2	1.5	94.1
4	BisILs-C$_8$H$_{17}$-W2	1.5	95.5
5	BisILs-C$_{12}$H$_{25}$-W2	1.5	87.9
6	BisILs-C$_6$H$_5$CH$_2$-W2	1.5	88.5
7	TriILs-CH$_3$-W2	1.5	91.0

[a] Reaction conditions: 1.5 mol% of catalyst (W), 1.1 equiv of H$_2$O$_2$, were stirred at room temperature.
[b] Isolated yields (average in two runs).
[c] The catalyst was reported in literature [34].

3.3.2. The influence of N-end-capped alkyl groups on the catalytic ability

The experimental results also show that the end-capped alkyl groups on the imidazole ring affect the reaction significantly. From Table 2 the catalyst with n-octyl as the terminal alkyl group is the most effective for the oxidation reaction as it affords the highest product yield (entry 4). The catalysts with methyl, n-butyl, benzyl or n-dodecyl are less reactive. These results indicate that the catalysts bearing more or less than eight carbons in the chain of alkyl group are less effective. This may be because the octyl group is more efficient in balancing the critical hydrophobic and hydrophilic parameters and thus provides a suitable hydrophobic and hydrophilic environment for substrates to move into the brushes where the catalytically active species is attached and for the product and byproduct (water) to move out of the brushes. As for benzyl, its rigid structure makes it difficult for the reagents to approach the catalytically active site.

3.4. Catalytic abilities of catalyst BisILs-C$_8$H$_{17}$-W2
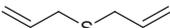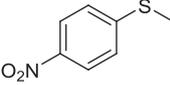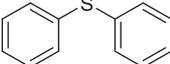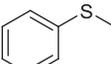
3.4.1. Oxidation of sulfides to sulfoxides

The catalyst BisILs-C$_8$H$_{17}$-W2 showed the best catalytic activity in all of the catalysts. Therefore, this catalyst was applied to the oxidation of other various sulfides with aqueous H$_2$O$_2$ (Table 3). The data in Table 3 displayed that both aromatic and aliphatic sulfoxides could be obtained in high yields. Meanwhile, only trace amounts of over-oxidation products of sulfones were detected by GC after reaction. Control experiments indicate that in the absence of the catalyst, the oxidation of thioanisole at the same condition gives methyl phenyl sulfoxide in a rather low yield of 18.3%, which indicated that the catalyst played important role in the reaction.

Compared with a previous report about using an ordinary silica-based tungstate catalyst [38], the amount of H$_2$O$_2$ needed in the catalytic oxidation system was reduced greatly from 3 equivalents to 1.1 equivalents (based on the amount of sulfide). The catalyst provides excellent chemoselectivity for sulfides containing other functional groups that are susceptible to oxidation. For instance,

Table 3

The catalytic ability of catalyst BisILs-C_8H_{17}-W2 in oxidation of sulfide to sulfoxide.[a]

$$R{-}S{-}R' \xrightarrow[\text{catalyst}]{CH_2Cl_2 : CH_3OH,\ 30\%\ H_2O_2,\ rt} R{-}S(O){-}R'.$$

Entry	Sulfide	Time (h)	Conv. (%)	Yield (%)[b]
1		1.0	99.8	89.2
2		1.5	100	90.0
3		1.5	99.2	92.2
4		4.0	94.6	89.9
5		4.0	93.7	83.1
6		1.5	98.6	95.5

[a] Reaction conditions: 1.5 mol% of catalyst (W), 1.1 equiv of H_2O_2, were stirred at room temperature.
[b] Isolated yields (average in two runs).

allyl methyl sulfoxide and allyl sulfoxide were obtained in high yields of 92.2% and 90.0%, respectively, and no epoxidation products were detected by GC. In addition, the yield of diphenyl sulfoxide was lower than that of methyl phenyl sulfoxide because of steric effects. Although the strong electron withdrawing group NO_2 is present in the phenyl ring of these sulfides, the sulfoxide yield was not affected.

3.4.2. Oxidation of sulfides to sulfones

When the molar ratio of the catalyst:H_2O_2:sulfide was changed from 1.5:110:100 to 2:250:100, the sulfones were obtained at room temperature within 5 h (Table 4). From Table 4, the BisILs-C_8H_{17}-W2 catalyst gave high catalytic activity in all the reactions and the conversion of sulfides were all 100% without exception. Similar to the oxidation of sulfides to sulfoxides, unsaturated double bonds are also tolerated during these reactions where aqueous hydrogen peroxide was used in large excess. This result further showed that

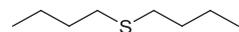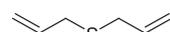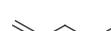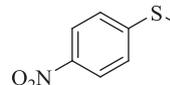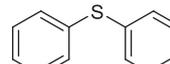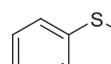the catalytic oxidation system possesses excellent chemoselectivity.

3.4.3. The recycling of catalyst BisILs-C_8H_{17}-W2

It is noteworthy that the work-up of the reaction mixture is rather simple since the catalyst can be recovered by simple filtration. The recovered catalyst is capable of being reused in subsequent cycles. Eight consecutive preparations of the methyl phenyl sulfoxide showed no significant loss in yield (Table 5), which indicates that the catalytic activity of the catalyst did not change significantly compared with the fresh catalyst. In each case, the catalyst was recovered by filtration, washing with ethanol and water, and the experiment repeated. ICP-MS analysis of the reaction solution after filtration of the brushes shows that only 0.58 mg/l tungsten was present, which indicates that there is almost no loss of metal components.

Table 4

The catalytic ability of catalyst BisILs-C_8H_{17}-W2 in oxidation of sulfide to sulfone.[a]

$$R{-}S{-}R' \xrightarrow[\text{catalyst}]{CH_2Cl_2 : CH_3OH,\ 30\%\ H_2O_2,\ rt} R{-}SO_2{-}R'.$$

Entry	Sulfide	Time (h)	Yield (%)[b]
1		2.5	96.2
2		3.0	92.8
3		2.5	86.5
4		2.5	90.8
5		5.0	85.3
6		5.0	80.6
7		4.0	98.8

[a] Reaction conditions: 2 mol% of catalyst (W), 2.5 equiv of H_2O_2, were stirred at room temperature.
[b] Isolated yields (average in two runs).

Table 5
The recycling of BisILs-C$_8$H$_{17}$-W2 (Runs 1-10) in the oxidation of methyl phenyl sulfides to sulfoxides.[a]

Cycle	1	2	3	4	5	6	7	8
Yield[b] (%)	95.5	93.7	94.9	92.6	90.9	90.1	92.3	91.7

[a] Reaction conditions: 1.5 mol% of catalyst (W), 1.1 equiv of H$_2$O$_2$, were stirred at room temperature.
[b] Isolated yields (average in two runs).

4. Conclusions

We developed an environmentally benign catalyst for the selective oxidation of sulfides to corresponding sulfoxides and sulfones with dilute H$_2$O$_2$, an ideal oxidant. Catalyst/product separation is very simple and the catalyst recovered after the reaction is reusable as it retains its catalytic performance. The catalyst assembles the ionic liquid, the PTC and the peroxo-tungstates together and is shown to be highly efficient and recyclable. Because of its high recyclability and the use of hydrogen peroxide as the oxidant, this catalyst has environmental and economic advantages over other supported catalysts. In addition, the advantages of this catalytic oxidation system also includes high product yields, high substrate conversion, short reaction time as well as improved catalytic activity because more active species are present and a richer medium environment is produced.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.03.024.

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