Polyoxometalate-based protic alkylimidazolium salts as reaction-induced phase-separation catalysts for olefin epoxidation†

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Two protic alkylimidazolium polyoxometalates, together with two corresponding aprotic N-methyl-alkylimidazolium polyoxometalates were synthesized and characterized by the methods of NMR, IR and TGA *etc*. Then, these salts were employed as catalysts for the epoxidation of cyclooctene in different media. The novel protic N-dodecylimidazolium peroxotungstate $[HDIm]_2[\{W=O(O_2)_2\}_2(\mu–O)]$ was found to be a room temperature liquid molten salt (ionic liquid) and the most effective catalyst for the epoxidation of cyclooctene among these salts. The ionic liquid catalyst $[HDIm]_2[\{W=O(O_2)_2\}_2(\mu–O)]$ can also be extended to the epoxidation of some other substrates. On the basis of this experimental observation, an efficient reaction-induced phase-separation catalyst system has been developed in this work. The reaction system can switch from tri-phase to emulsion and then to biphase and finally to all the catalyst self-precipitating at the end of the reaction, which made the recovery and reuse of the present catalyst very convenient.

Introduction

Ionic liquids (ILs) are receiving increasing attention from both industry and academics, and research involving ILs is expanding to many different areas of knowledge. A subset of ILs are protic ionic liquids (PILs),[1] which are easily produced through the combination of a Brønsted acid and a Brønsted base. PILs have a number of unique properties compared to other aprotic ILs. For example, the PILs can promote metal-assisted catalytic processes like dimerisation of methyl acrylate, selective dimerization of α–methylstyrene, ring closing metathesis, and thus lead to significant improvements both in activity and selectivity.[2] PILs have shown high polarity as well, especially the PILs formed from the N-alkylimidazolium cation with the stronger acids showed higher polarities, which may have some significant effects on the catalytic reaction.[3]

Recently, a variety of functionalized ILs which have functional groups tethered to their cations or anions have been developed,[4] but most of them have been designed for the functionalization of cations, especially the incorporation of functional groups into the imidazolium cations, while less attention has been paid to the functionality of anions. Definitely, the emergence of anion-functionalized ILs will endow the ILs with huge diversity both in quantity and properties and with more space for further development.

The transition metal peroxo complexes are very important in the fields of structural chemistry, biological chemistry, catalysis, and material science.[5] Among them, tungsten peroxo complexe-based oxidation systems with H_2O_2 have attracted much attention because of the high reactivity and inherent poor activity for the decomposition of H_2O_2. To date, μ–η^1: η^1–peroxo–bridged dinuclear peroxotungstate $[\{W=O(O_2)_2\}_2(\mu–O)]^{2-}$ (also formulated as $[W_2O_{11}]^{2-}$) is one of the well defined dimeric peroxotungstates,[6] and its structure has been characterized crystallographically in detail in its K^+ or tetraalkylammonium salt.[7] Although the dinuclear peroxotungstate $[W_2O_{11}]^{2-}$ could act as a homogeneous catalyst in water or organic solvents for the epoxidation of olefins or allylic alcohols using hydrogen peroxide,[7,8] the recycling of the dinuclear tungsten catalyst has been rarely investigated.[9]

Effective catalyst separation, leading to minimum waste, is one of the underlying goals of green chemistry. While homogeneous catalysts are available for the catalytic reactions, it is often quite difficult to separate the catalyst from the products, while ILs as successful alternative solvents for homogeneous biphasic catalysis have been designed for immobilizing catalysts, facilitating product isolation and recycling of the catalyst system. In this context, we will focus on the synthesis and catalytic application of the molten salts which can be obtained by pairing alkylimidazolium cations with a widely used catalytically active peroxotungstate anion.

The main aim of this work is to develop a simplified approach where the catalyst can be easily separated from the products. Herewith, we present four alkylimidazolium polyoxometalates, and two of them are protic salts. These salts have been utilized as catalysts for the epoxidation of olefins for the first time and, especially, the protic salt N-dodecylimidazolium peroxotungstate $[HDIm]_2[\{W=O(O_2)_2\}_2(\mu–O)]$ is found to be a room temperature IL and can be used as a reaction-induced phase-separation catalyst, which leads to easy separation of the catalyst from the products *via* simple decantation.

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Results and discussion

Catalyst preparation and characterization

The protic N-dodecylimidazolium peroxotungstate $[HDIm]_2[W_2O_{11}]$ and N-hexylimidazolium peroxotungstate $[HHIm]_2[W_2O_{11}]$ were synthesized by the protonation of the corresponding alkylimidazoles, respectively,[10] and then by pairing the protic alkylimidazolium cations with catalytically active $[W_2O_{11}]^{2-}$ anion under acidic conditions. Two other aprotic salts, 1-hexyl-3-methyl-imidazolium peroxotungstate $[HMIm]_2[W_2O_{11}]$ and 1-dodecyl-3-methyl-imidazolium peroxotungstate $[DMIm]_2[W_2O_{11}]$, were also synthesized to compare with their protic analogues, respectively. The synthesized catalysts are represented in Fig. 1 and their
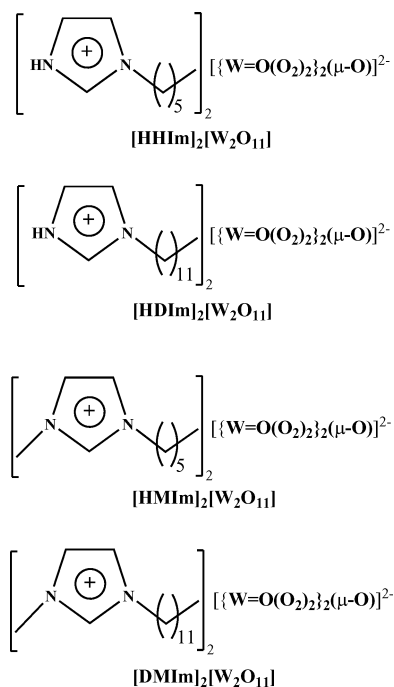
$$\left[\overset{HN}{\underset{}{\bigoplus}} N \diagdown_5 \right]_2 [\{W=O(O_2)_2\}_2(\mu\text{-}O)]^{2-}$$

$[HHIm]_2[W_2O_{11}]$

$$\left[\overset{HN}{\underset{}{\bigoplus}} N \diagdown_{11} \right]_2 [\{W=O(O_2)_2\}_2(\mu\text{-}O)]^{2-}$$

$[HDIm]_2[W_2O_{11}]$

$$\left[\overset{}{\underset{}{\bigoplus}} N \diagdown_5 \right]_2 [\{W=O(O_2)_2\}_2(\mu\text{-}O)]^{2-}$$

$[HMIm]_2[W_2O_{11}]$

$$\left[\overset{}{\underset{}{\bigoplus}} N \diagdown_{11} \right]_2 [\{W=O(O_2)_2\}_2(\mu\text{-}O)]^{2-}$$

$[DMIm]_2[W_2O_{11}]$

Fig. 1 The anion $[W_2O_{11}]^{2-}$ functionalized catalysts.

structures have been proved by NMR and IR. The two salts $[HDIm]_2[W_2O_{11}]$ and $[DMIm]_2[W_2O_{11}]$ were proved to be amorphous state according to XRD (Figure S1, ESI)† and their thermal stability was characterized by TGA (Figure S2, ESI).† In the following step, the synthesized catalysts were employed for olefin epoxidation and a new approach to recycle the PIL $[HDIm]_2[W_2O_{11}]$ catalyst was demonstrated.

Epoxidation of cyclooctene in different solvents

The epoxidation of cyclooctene was chosen as the model reaction in different solvents using 30% aqueous H_2O_2 with the four catalysts $[HHIm]_2[W_2O_{11}]$, $[HDIm]_2[W_2O_{11}]$, $[HMIm]_2[W_2O_{11}]$ and $[DMIm]_2[W_2O_{11}]$. As shown in Table 1, the selectivities to cyclooctane epoxide were all found to be higher than 99% and the catalytic activities of the N-dodecylimidazolium catalysts were superior to those of the corresponding N-hexylimidazolium ones in different solvents. Water, EtOAc and CH_2Cl_2 were found to be poor solvents for the epoxidation with all four catalysts (entries 1–4). Interestingly, the PIL $[HDIm]_2[W_2O_{11}]$ was the most efficient catalyst for the epoxidation in different media, especially in polar organic solvents such as CH_3CN and CH_3OH (entries 5 and 6) where the conversions can reach 97.2% and 100%, respectively, which indicated that the solvents had a significant effect on the polyoxometalate catalysts, as observed by several research groups previously.[11]

To make the synthesis greener, the mixed solvents with different volume ratios of CH_3OH to H_2O as reaction media were screened for the epoxidation. Surprisingly, the activity was still very excellent, especially by using the $[HDIm]_2[W_2O_{11}]$ or $[DMIm]_2[W_2O_{11}]$ catalysts when the volume ratio of CH_3OH to H_2O was kept at 1:3 (Table 1, entry 7). Considering the excellent conversion of cyclooctene by using the IL $[HDIm]_2[W_2O_{11}]$ catalyst in CH_3OH, we investigated the reaction kinetics over the $[HDIm]_2[W_2O_{11}]$ and $[DMIm]_2[W_2O_{11}]$ catalysts in CH_3OH or CH_3OH–H_2O medium (volume ratio = 1:3) (Fig. 2). It can be seen that the $[HDIm]_2[W_2O_{11}]$ catalyst gave a higher reaction rate than $[DMIm]_2[W_2O_{11}]$ in the mixed solvent of CH_3OH–H_2O. On the other hand, the reaction rate was apparently higher

Table 1 Epoxidation of cyclooctene with the four synthesized catalysts in different solvents[a]

$$\text{Catalyst, } H_2O_2 \atop \text{Solvent, 333K, 4h}$$

| Entry | Solvents | Con.(%)[b] | | | |
		$[HHIm]_2[W_2O_{11}]$	$[HDIm]_2[W_2O_{11}]$	$[HMIm]_2[W_2O_{11}]$	$[DMIm]_2[W_2O_{11}]$
1	None	24.3	65.9	38.8	41.0
2	H_2O	15.9	64.5	12.6	27.8
3	EtOAc	41.8	54.4	14.3	19.5
4	CH_2Cl_2	55.0	79.1	5.4	52.4
5	CH_3CN	59.4	97.2	12.6	28.7
6	CH_3OH	66.2	100	4.3	46.5
7	CH_3OH–H_2O	54.4	100	26.2	100

[a] Cyclooctene (1.5 mmol), catalyst (30 μmol, 2 mol%), 30% aqueous H_2O_2 (0.5 mmol), solvent (1 ml), 333 K, 4 h. Conversion and selectivity were determined by GC analysis. [b] Conversion (%) = products (mol)/initial H_2O_2 (mol) × 100%, selectivity of all the epoxide products were >99%. CH_3OH:H_2O = 1:3 (volume ratio).
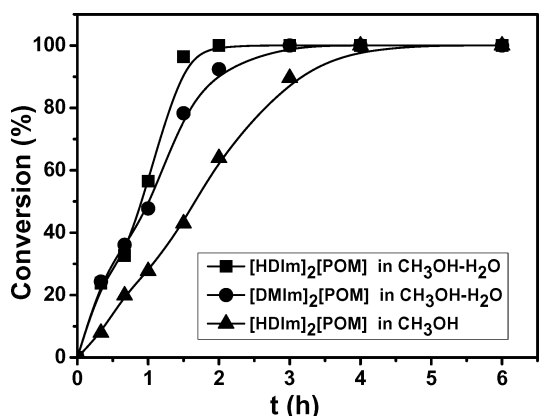
Fig. 2 Conversion as a function of time during the cyclooctene epoxidation at 60 °C over ILs in CH_3OH or $CH_3OH–H_2O$ (volume ratio = 1:3) reaction medium.

in the mixed solvent of $CH_3OH–H_2O$ than in the single CH_3OH medium with $[HDIm]_2[W_2O_{11}]$ as catalyst.

Notably, the present reaction system switching from tri-phase to biphase during the epoxidation reaction, and then to all the catalyst self-precipitating at the end of reaction was observed visually using $[HDIm]_2[W_2O_{11}]$ in $CH_3OH–H_2O$ medium (Fig. 3). Before the reaction, the PIL catalyst deposited at the bottom of the flask and there were three separate phases in the flask (Fig. 3a). At the beginning of the reaction, emulsification of the system was observed for a very short period of time (Fig. 3b), but during the reaction there were two phases separated with the catalyst all dissolved in the substrate while the mixed solvent was almost transparent (Fig. 3c), and at the end of the reaction all the catalyst self-precipitated at the bottom when the H_2O_2 was used up. Meanwhile, the liquid phase was kept clear. Since the catalyst can self-precipitate from the system at the end, the separation and reuse of the catalyst were very convenient. In contrast, although the IL $[DMIm]_2[W_2O_{11}]$ also showed excellent activity for the epoxidation of cyclooctene (Table 1, entry 7), it was found that the $[DMIm]_2[W_2O_{11}]$ catalyst
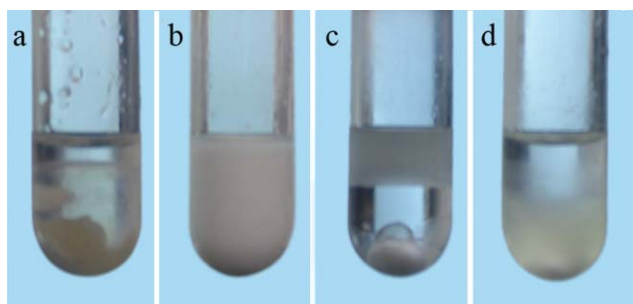

Fig. 3 Photograph of the epoxidation of cyclooctene over the $[HDIm]_2[W_2O_{11}]$ catalyst in the mixed solvent of $CH_3OH–H_2O$ (volume ratio = 1:3). a) $[HDIm]_2[W_2O_{11}]$ (pale yellow viscous liquid at the bottom), mixed solvent of $CH_3OH–H_2O$ (transparent liquid in the middle), cyclooctene (transparent liquid in the upper layer); b) emulsification of the system after reaction for 10 min; c) biphasic system was observed after reaction for 1 h with the catalyst dispersed in the substrate phase while the mixed solvent was transparent; d) at the end of the reaction, the pale yellow IL catalyst self-precipitated at the bottom of the flask. Note: the amounts of substrate and IL catalyst have been tripled for visual clarity.

Table 2 Recycling of the IL $[HDIm]_2[W_2O_{11}]$ in different solvents[a]

Run	Con.(%)				
	CH_3OH	CH_3CN	None	$[BMIm][PF_6]$	$CH_3OH–H_2O$
1	100	97.2	65.9	76.0	100
2	81.2	91.0	56.3	69.8	100
3	7.4	68.3	39.6	61.2	100
4	—	49.7	—	57.1	100
5	—	38.8	—	—	99.8
6	—	—	—	—	99.6

[a] Reaction conditions: cyclooctene (1.5 mmol), catalyst (30 μmol, 2 mol%), 30% aqueous H_2O_2 (0.5 mmol), solvent (0.4 ml), 333 K, 4 h. Conversion (%) = products (mol)/initial H_2O_2 (mol) × 100%. The selectivities to cyclooctane epoxides were all >99%. $CH_3OH:H_2O$ = 1:3 (volume ratio).

was still dissolved in the mixed medium after the reaction instead of self-precipitating, so the recovery of the catalyst was very difficult.

Recycling of the IL $[HDIm]_2[W_2O_{11}]$

The recyclability of the IL catalyst $[HDIm]_2[W_2O_{11}]$ has been investigated by choosing the epoxidation of cyclooctene as a model reaction in several solvents. As shown in Table 2, in the medium of $CH_3OH–H_2O$, after each reaction, all the IL catalyst can self-precipitate and then it can be easily recovered by decantation. The subsequent analysis of the decantate by ICP-AES showed that only 20 ppm of W content was leached. This indicated that the loss of the IL catalyst was neglectable during catalytic recycles. In addition, the conversion of cyclooctene still remain 99.6% with >99% selectivity even after six consecutive cycles. However, the conversions dropped rapidly even after the first or second cycle in organic solvents, such as CH_3OH, CH_3CN. These results were in accord with the observation that the $[HDIm]_2[W_2O_{11}]$ catalyst was found to be leaching out considerably during catalytic recycles. Moderate conversions with the conventional IL $[BMIm][PF_6]$ as the reaction medium or without solvent were obtained in the first run, 76.0% and 65.9%, respectively, although the conversion dropped more slowly in $[BMIm][PF_6]$ during the consecutive catalytic recycles.

Epoxidation of various olefins by IL $[HDIm]_2[W_2O_{11}]$

As we were encouraged by the good activity, selectivity and stability obtained by using $[HDIm]_2[W_2O_{11}]$ as a catalyst for the epoxidation of cyclooctene, the IL catalyst was extended to the epoxidation of other alkenes. As shown in Table 3, the IL catalyst could be applicable to the epoxidation of both olefins and allylic alcohols with 30% H_2O_2 as an oxidant. In the mixed solvent of $CH_3OH–H_2O$, cyclooctene was converted into the corresponding epoxide completely within 2 h with 99.9% selectivity (entry 1), while other olefins chosen in this work were epoxidized mainly into the corresponding hydrolysis products. For example, cyclohexene was transformed into the hydrolysis product (cyclohexane-1,2-diol) from the corresponding epoxide with excellent conversion (99.0%) and moderate selectivity (66.3%) (entry 2). Styrene was less activated with 84.4% conversion and 61.2% selectivity to styrene-1,2-diol

Table 3 Epoxidation of various substrates catalyzed by $[HDIm]_2[W_2O_{11}]$ in the mixed solvent of $CH_3OH–H_2O^a$

Entry	Substrates	Time (h)	Con.(%)	Sel.(%)
1	Cyclooctene	2	100	99.9
2	Cyclohexene	4	99.0	66.3[b]
3	Cyclohexene[c]	4	86.3	92.0
4	Styrene	4	84.4	61.2[d]
5	1-Hexene	10	6.2	99.1[e]
6	3-Methyl-2-buten-1-ol	0.5	94.4	99.0
7	Geraniol	2	88.6	99.6

^{a} Reaction conditions: substrate (1.5 mmol), catalyst (30 μmol, 2 mol%), 30% aqueous H_2O_2 (0.5 mmol), solvent (1 mL, the volume ratio of CH_3OH to H_2O was 1:3), 333 K, the analysis of products were performed by GC and GC-MS. Conversion (%) = products (mol)/initial H_2O_2 (mol) × 100%. ^{b} The main product is cyclohexane-1,2-diol; the others were cyclohexanol and cyclohexanone. ^{c} The reaction was carried out in CH_3CN and the product was mainly cyclohexane epoxide. ^{d} The main product was styrene-1,2-diol, the others were benzaldehyde and benzoic acid. ^{e} The product was hexane-1,2-diol.

(entry 4), while 1-hexene was converted into the hexane-1,2-diol with only 6.2% conversion even after 10 h reaction (entry 5), which was all in accord with the electrophilic mechanism of the epoxidation. Cyclohexene was selectively transformed into cyclohexane epoxide in single CH_3CN medium (entry 3), while it formed cyclohexane-1,2-diol in the mixed solvent by catalytic hydrolysis of the epoxide ring of cyclohexene oxide, which revealed the effect of H_2O on the product selectivity in the presence of the acidic PIL $[HDIm]_2[W_2O_{11}]$ catalyst. On the other hand, the different selectivities to diol or epoxide obtained with cyclohexene and cyclooctene as substrates could be explained due to the higher hydrophilicity of cyclohexane epoxide, compared with that of cyclooctane epoxide. It is noteworthy that the reaction activities of allylic alcohols were higher than those of olefins, which was proved by the facts that 3-methyl-2-buten-1-ol and geraniol were converted nearly completely to the corresponding epoxides within 0.5 and 2 h, respectively, while the complete conversion of olefins normally needed more than 2 h. For the epoxidation of geraniol, GC-MS analysis indicated that the 2,3-epoxide was the only product. Since geraniol is an allylic alcohol which has two possible sites of epoxidation attack, namely the two double bonds, according to the reported mechanism, the catalyst should favor epoxidation at the C6–C7 position. But it was demonstrated that the 2,3-epoxide was the only product, therefore we suggest the presence of an intermediate complex involving the metal centre, the oxidant and the substrate, that may coordinate through the –OH group of the allylic alcohol.[7b,12]

Conclusion

In summary, we have synthesized four polyoxometalate anion-functionalized catalysts. The length of the alkyl chain in the imidazolium cation played an important role in effecting the reaction. The PIL N-dodecylimidazolium peroxotungstate $[HDIm]_2[W_2O_{11}]$ was proved to be the most active catalyst among them for the epoxidation of olefins and allylic alcohols. Furthermore, the $[HDIm]_2[W_2O_{11}]$ catalyst can be regarded as a reaction-induced phase-separation catalyst. The catalytic system switched the reaction mixture from tri-phase to emulsion,

then to biphase, and finally to all the catalyst self-precipitating from the reaction medium after the reaction. It combined the advantages of an homogeneous catalyst during the reaction with an heterogeneous catalyst of easy separation after the reaction. So the catalyst can be easily separated by decantation and reused for at least six times, which provided an effective approach to circumvent the difficulty in separating homogeneous epoxidation catalysts from the products.

Experimental

General remarks

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. CH_2Cl_2 and DMF (A.R. grade) were distilled from CaH_2 prior to use. CH_3CN and CH_3OH (A.R. grade) were distilled from molecular sieves (4Å). Commercially available 30% H_2O_2, EtOAc, cyclohexene, styrene, 3-methyl-2-buten-1-ol and geraniol were purchased from Sinopharm Chemical Reagent Co. Ltds and used without further purification. *cis*-Cyclooctene and 1-hexene were purchased from Alfa Aesar. $[BMIm][PF_6]$ was synthesized using the procedure reported by other authors[13] and $K_2[\{W=O(O_2)_2\}_2(\mu–O)]$ was prepared as a white crystal according to ref. 6a, v_{max}/cm^{-1} 965.9(WO), 854.0(OO), 762.8(W_2O), 614.9(W(O_2)), 552.2(W(O_2)).

All NMR spectra were recorded on a Bruker Avance 500 instrument (500 MHz ^{1}H, 125 MHz ^{13}C) using $CDCl_3$ and TMS as solvent and reference, respectively. Chemical shifts (δ) were given in parts per million and coupling constants (J) in hertz. FT-IR spectra were recorded at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna 550). The products were analyzed by GC and GC-MS equipped with a HP–5 MS column (30 m length, 0.25 mm i.d). The elemental analysis of C, H, N was performed on an Elementar Vario EI III Elementa and ICP-AES analysis of W on TJA IRIS 1000 instrument, respectively.

Synthesis of protic ionic liquid (PIL) N-dodecylimidazolium peroxotungstate $[HDIm]_2[\{W=O(O_2)_2\}_2(\mu–O)]$ (abbreviated as $[HDIm]_2[W_2O_{11}]$)[10]

The synthesis of dodecyl methanesulfonate. A solution of 1-dodecanol (7.45 g, 40 mmol) and triethylamine (7.77 mL, 56 mmol) in dichloromethane (30 ml) was cooled in an ice bath as methanesulfonyl chloride (3.56 mL, 46 mmol) in dichloromethane (10 ml) was added. An external water bath was used to control the reaction mixture temperature between 10–20 °C. After addition, stirring was continued for further 2 h. Then water (25 ml) was added, the aqueous layer containing the triethylammonium chloride by-product was separated; the organic layer was washed sequentially with a saturated solution of $NaHCO_3$, water and then dried with sodium carbonate. The solvent was evaporated under reduced pressure to afford the desired dodecyl methanesulfonate, as a colorless liquid (9.8 g, 93%).

The synthesis of N-dodecylimidazole. Dodecyl methanesulfonate (9.8 g, 37.2 mmol) was dissolved in DMF (50 ml) and added to a solution of the sodium salt of imidazole formed by

reaction of imidazole (5.0 g, 74 mmol) with sodium hydride (2.66 g, 111 mmol) in DMF (50 ml). The mixture was heated to 60 °C for 6 h, cooled, and diluted with water and 6 N HCl. Then it was extracted with EtOAc. The extract was washed with brine and water, and then dried with sodium carbonate. The solvent was evaporated under reduced pressure to afford N-dodecylimidazole as a pale yellow oil product (8.22 g, 94%); δ_H (500 MHz; CDCl$_3$): 0.88 (3H, t, Me), 1.27 (18H, m, C$_9$H$_{18}$), 1.75 (2H, m, CH$_2$), 3.90 (2H, t, CH$_2$), 6.86 (1H, s, CH), 7.05 (1H, s, CH), 7.45 (1H, s, CH).

The synthesis of protic N-dodecylimidazolium tetrafluoroborate [HDIm][BF$_4$]. N-dodecylimidazole (8.22 g, 35 mmol) in ether (10 ml) was placed in a flask, which was stirred and cooled to 0 °C. Then tetrafluoroboric acid (8.09 g, 35 mmol, 38% solution in water) was added dropwise while stirring and cooling to maintain the temperature at 0–5 °C. The reaction mixture was stirred for an additional period of 1 h. It was washed with water and then dried under reduced pressure to afford the colorless oil product protic N-dodecylimidazolium tetrafluoroborate [HDIm][BF$_4$] (10.66 g, 94%); ν_{max}/cm^{-1} 2967.3, 2937.4 and 2853.7(CH), 1634.9(CN), 1574.6(CC), 1465.9 and 1377.6(CH$_2$–H), 1082.81(BF$_4^-$); δ_H (500 MHz; CDCl$_3$): 0.77 (3H, t, CH$_3$), 1.24 (18H, m, C$_9$H$_{18}$), 1.86 (2H, m, CH$_2$), 4.18 (2H, t, CH$_2$), 7.18 (1H, s, CH), 7.46 (1H, s, CH), 8.65 (1H, s, CH), 12.42 (1H, s, H).

The synthesis of PIL N-dodecylimidazolium peroxotungstate [HDIm]$_2$[W$_2$O$_{11}$]. PIL N-dodecylimidazolium peroxotungstate [HDIm]$_2$[W$_2$O$_{11}$] was prepared conveniently by anion exchange. Under stirring, to protic dodecylimidazolium tetrafluoroborate [HDIm][BF$_4$] (10.66 g, 33 mmol) in CH$_2$Cl$_2$ was added the powder of K$_2$[{W=O(O$_2$)$_2$}$_2$(μ–O)] (10.23 g, 16.45 mmol), the mixture was treated at room temperature for 12 h and then repeated another two times. After the reaction, the liquid was separated by filtration and the solvent was evaporated under reduced pressure to afford a slightly yellow, highly viscous liquid (16.14 g, 90%) as a product (Found: C, 35.89; H, 5.84; N, 5.58; W 33.68%. C$_{30}$H$_{58}$N$_4$O$_{11}$W$_2$ requires C, 35.38; H, 5.74; N, 5.50; W, 36.10%); ν_{max}/cm^{-1} 2956.1, 2923.8 and 2853.1(CH), 1634.7(CN), 1575.6(CC), 1465.6 and 1376.8(CH), 1088.6(BF$_4^-$), 960.2(W=O), 874.2(OO), 724.4(W$_2$O)), 629.2 and 543.0(W(O$_2$)); δ_H (500 MHz; CDCl$_3$): 0.85 (3H, t, CH$_3$), 1.20 (18H, m, C$_9$H$_{18}$), 1.86 (2H, m, CH$_2$), 4.20 (2H, t, CH$_3$), 7.14 (1H, s, CH), 7.45 (1H, s, CH), 8.70 (1H, s, CH); δ_C (125 MHz; CDCl$_3$): 14.78, 23.36, 27.03, 29.60, 29.77, 30.04, 30.15, 30.28, 30.33, 31.02, 32.59, 50.08, 121.24, 122.05, 136.10. m/z (EI) 237.2(M$^+$).

Synthesis of protic N-hexylimidazolium peroxotungstate [HHIm]$_2$ [{W=O(O$_2$)$_2$}$_2$(μ–O)] (abbreviated as [HHIm]$_2$[W$_2$O$_{11}$])

The PIL N-hexylimidazolium peroxotungstate ([HHIm]$_2$-[W$_2$O$_{11}$]) was obtained in a similar way as that of the IL catalyst [HDIm]$_2$[W$_2$O$_{11}$] except that 1-hexanol was used as the starting material instead of 1-dodecanol (Found: C, 25.68; H, 4.11; N, 6.65; W 40.82%. C$_{18}$H$_{34}$N$_4$O$_{11}$W$_2$ requires C, 25.43; H, 4.03; N, 6.59; W, 43.25%); ν_{max}/cm^{-1} 2957.4, 2932.5 and 2860.2(CH), 1655.0(CN), 1571.7(CC), 1466.9 and 1379.5(CH), 1053.7(BF$_4^-$),

960.2(WO), 877.89(OO), 724.4(W$_2$O)), 627.6 and 533.7(W(O$_2$)); δ_H (500 MHz; CDCl$_3$): 0.88 (3H, t, CH$_3$), 1.27 (6H, m, C$_3$H$_6$), 1.83 (2H, m, CH$_2$), 4.09 (2H, t, CH$_2$), 7.08 (1H, s, CH), 7.21 (1H, s, CH), 8.13 (1H, s, CH); δ_C (125 MHz; CDCl$_3$) 14.42, 22.93, 26.67, 30.17, 31.70, 47.49, 119.25, 129.77, 137.52.

Synthesis of N-methyl dodecylimidazolium peroxotungstate [DMIm]$_2$[{W=O(O$_2$)$_2$}$_2$(μ–O)] (abbreviated as [DMIm]$_2$[W$_2$O$_{11}$])

The synthesis of N-methyl dodecylimidazolium methanesulfonate. Dodecyl methanesulfonate (9.8 g, 37 mmol) was mixed with 1-methylimidazole (3.03 g, 37 mmol) and the reaction mixture was kept at room temperature for 12 h, then raised to 60 °C for 48 h with vigorous stirring. After reaction, the product was recrystallized at 0 °C three times using ethyl acetate as solvent (20 ml × 3). Then after vacuum drying, pale yellow liquid N-methyl dodecylimidazolium methanesulfonate was obtained (10.28 g, 80%); δ_H (500 MHz; CDCl$_3$) 0.77 (3H, t, CH$_3$), 1.20 (18H, m, C$_9$H$_{18}$), 1.81 (2H, m, CH$_2$), 2.70 (3H, s, CH$_3$), 3.86 (3H, s, CH$_3$), 4.18 (2H, t, CH$_2$), 7.44 (1H, s, CH), 7.46 (1H, s, CH), 8.78 (1H, s, CH).

The synthesis of N-methyl dodecylimidazolium peroxotungstate [DMIm]$_2$[W$_2$O$_{11}$]. N-methyl dodecylimidazolium peroxotungstate [DMIm]$_2$[W$_2$O$_{11}$] was prepared conveniently by anion exchange. Under stirring, to [DMIm][CH$_3$SO$_3$] (10.28 g, 29.6 mmol) in CH$_2$Cl$_2$ (15 ml) was added the powder of K$_2$[{W=O(O$_2$)$_2$}$_2$(μ–O)] (9.73 g, 14.8 mmol), the mixture was treated at room temperature for 12 h and then repeated another two times. After the reaction, the liquid was separated by filtration and the solvent was evaporated under reduced pressure to afford a colorless powder (14.84 g, 90%) as a product (Found: C, 36.79; H, 6.01; N, 5.11; W 34.99%. C$_{32}$H$_{62}$N$_4$O$_{11}$W$_2$ requires C, 36.73; H, 5.97; N, 5.35; W, 35.13%); ν_{max}/cm^{-1} 3063.1, 2917.4 and 2852.1(CH), 1631.3(CN), 1572.1(CC), 1472.1 and 1382.6(CH), 1178.9(MeN), 936.7(WO), 864.9(OO), 729.9(W$_2$O), 622.7 and 535.2(W(O$_2$)); δ_H (500 MHz; CDCl$_3$) 0.89 (3H, t, CH$_3$), 1.24 (18H, m, C$_9$H$_{18}$), 1.78 (2H, m, CH$_2$), 4.00 (3H, s, CH$_3$), 4.19 (2H, t, CH$_2$), 7.17 (1H, s, CH), 7.56 (1H, s, CH), 9.59 (1H, s, CH); δ_C (125 MHz; CDCl$_3$) 14.78, 23.36, 27.16, 30.07, 30.31, 30.38, 30.38, 30.38, 30.43, 31.21, 32.61, 37.13, 50.35, 121.79, 124.75, 139.38.

Synthesis of N-methyl hexylimidazolium peroxotungstate [HMIm]$_2$[{W=O(O$_2$)$_2$}$_2$(μ–O)] (abbreviated as [HMIm]$_2$[W$_2$O$_{11}$])

The catalyst N-methyl hexylimidazolium peroxotungstate ([HMIm]$_2$[W$_2$O$_{11}$]) was synthesized in a similar way as that of the catalyst [DMIm]$_2$[W$_2$O$_{11}$] except that 1-hexanol was used as the starting material instead of 1-dodecanol (Found: C, 27.78; H, 4.59; N, 6.72; W, 38.94%. C$_{20}$H$_{38}$N$_4$O$_{11}$W$_2$ requires C, 27.35; H, 4.36; N, 6.38; W, 41.87%); ν_{max}/cm^{-1} 3062.6, 2918.7 and 2854.2(CH), 1633.2(CN), 1574.1(CC), 1473.6 and 1384.0(CH), 1196.5(MeN), 964.6(WO), 837.9(OO), 764.4(W$_2$O), 627.1 and 548.4(W(O$_2$)); δ_H (500 MHz; CDCl$_3$) 0.79 (3H, t, CH$_3$), 1.22 (6H, m, C$_3$H$_6$), 1.81 (2H, m, CH$_2$), 3.82 (3H, s, CH$_3$), 4.14 (2H, t, CH$_2$), 7.38 (1H, s, CH), 7.42 (1H, s, CH), 8.62 (1H, s, CH);

δ_C (125 MHz; CDCl$_3$) 14.42, 22.93, 26.67, 30.17, 31.70, 35.46, 47.49, 119.25, 129.77, 137.52.

General procedure for the epoxidation of olefins

Epoxidations were performed with the corresponding alkylimidazolium peroxotungstate in a 25 ml standard Schlenk tube. After 30 μmol catalyst was added, 0.5 mmol H$_2$O$_2$, 1.5 mmol substrate and 1 ml solvent was then charged into the Schlenk tube. The temperature was kept at 60 °C for the desired time. We define the GC selectivity of reaction products as the ratio of the epoxide moles to the total moles of all products.

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