Homogeneous epoxidation of lipophilic alkenes by aqueous hydrogen peroxide: catalysis of a Keggin-type phosphotungstate-functionalized ionic liquid in amphipathic ionic liquid solution†

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The ionic liquid compositions (**ILC**) composed of the Keggin-type phosphotungstate-functionalized ionic liquid of $[Dopy]_3[PW_{12}O_{40}]$ (**1**) and the amphipathic IL mixture of $[Bpy]BF_4$ and $[Dopy]BF_4$, were constructed as an effective catalytic system and ideal reaction medium for alkene epoxidation by aqueous H_2O_2, in which the real homogeneous catalysis was fulfilled with advantages of high activity, simplified work-up and available recyclability. The designing concept of the **ILC** and the IL effect on the activity/stability were discussed herein.

Introduction

Epoxidation of alkenes assumes significant importance since epoxides are one of the most valuable building blocks in the synthesis of various chemicals like perfumes, plasticizers, epoxy resins, drugs, sweeteners, *etc.* Many heterogeneous catalytic systems like microporous and mesoporous molecular sieves, layered-type materials, inorganic oxides, supported catalysts, zeolite encapsulated metal complexes, supported organometallic catalysts, and polyoxometalates[1–11] have been exploited for the epoxidation of alkenes. The design and fabrication of active and recyclable heterogeneous catalysts is still a challenging topic. Since most solid catalysts suffer from leaching of the active components and the severe mass transfer limitation while using them in liquid-phase selective oxidation.

Polyoxometalates (POMs) are metal-oxygen cluster anions (*i.e.* heteropolyanions) whose acidic and redox properties can be controlled by transition metal substitution and the counter-cations at molecular levels.[6–11] Alkene epoxidations using POMs as catalysts have been intensively studied because of the advantageous properties of POMs, such as relatively better tolerance to oxidative degradation, hydrostability, and their action as potential electron reservoirs.[6–11] The derived peroxoheteropoly species were believed to be the active intermediates.[12–14] And alkene epoxidations using aqueous hydrogen peroxide as terminal oxidant offer other advantageous merits. For example, hydrogen peroxide can oxidize organic compounds with relatively high atom efficiency and theoretically generate only water as a co-product. So, the use of POMs as catalysts and aqueous hydrogen peroxide (H_2O_2) as oxidant is qualified as a green processes. Anyway, when (hydrophilic) aqueous hydrogen peroxide was used as the oxidant in epoxidation of lipophilic alkenes which is catalyzed by a solid POM catalyst, the "triphase" catalysis occurs in the absence of phase transfer reagents and co-solvent as well. To solve these problems, the phase transfer catalysts like tetra(n-butyl)ammonium chloride and cetylpyridinium chloride were used in combination with POMs developed by Ishii and Venturello;[12] or the quaternary ammonium cations were introduced in POMs as the counter ions to match the required lipophilicity,[9,15–18] leading to the (partially) solubility of the resultant POMs in some polar organic solvents, such as acetonitrile, DMF, chlorohydrocarbons. However such homogeneous systems suffered from POM catalyst degradation,[13,14] non-recyclability,[19–22] and the usage of toxic organic solvents which largely defeated the significant environmental and economic advantages of using H_2O_2 as the oxidant.

The problems of heterogeneous systems with mass transfer limitation or homogeneous ones with unstable and non-recyclable catalysts in POM catalyzed epoxidation of alkenes evoked us to consider the use of the designable and recyclable ionic liquids (ILs). As alternative reaction media with non-volatile nature, tunable hydrophobicity and hydrophilicity, and flexible fabrication by the functional units, the room temperature ILs are given many advantages in minimizing solvent consumption, guaranteeing catalyst performance, and solving various organic/inorganic compounds, which facilitate the reaction efficiency in homogeneous phase, liquid–liquid separation and IL solvent-catalyst recycling, although their some properties like good chemical stability, volatility *etc.*, have been challenged.[23,24] By varying the cations and/or anions with specific functions that constitute IL's structure, it is possible to design abundant ILs with required functionalities.[25]

If the counter-anions in the common ILs like BF_4^-, PF_6^-, X^-, *etc.* were replaced by the heteropolyanions, the association of heteropolyanion anions with pyridinium (or imidazolium)-based cations could be regarded as the POM-functionalized ILs, which was reasonably believed to be (partially) soluble in the similar structured ILs due to the compatible ionophilicity

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and the similar building block of the organic cations. In addition, the hydrophilicity of aqueous H_2O_2 and the lipophilicity of alkenes urged us to develop an amphipathic IL system which can provide a suitable reaction environment for both hydrophilic and hydrophobic molecules. On the basis of these principles, the ionic compound associated with α-Keggin-type phosphotungstate anion ($[PW_{12}O_{40}]^{3-}$) and *n*-dodecyl pyridinium cation (**1**) was prepared and used as the catalyst in conjunction with N-*n*-butylpyridinium tetrafluoroborate ($[Bpy]BF_4$) and N-*n*-dodecylpyridinium tetrafluoroborate ($[Dopy]BF_4$) as the co-solvents. As for $[Dopy]BF_4$, which is in glassy state at room temperature, it is an amphipathic IL due to the presence of BF_4^- anion with hydrophilic nature and the long-chain dodecyl group in $[Dopy]^+$ cation with lipophilic nature. As for $[Bpy]BF_4$, it is a hydrophilic room temperature IL, which is suitable as the reaction medium. The mixture of $[Bpy]BF_4$ and $[Dopy]BF_4$ consequently resulted in the miscible room-temperature IL mixture with amphipathicity for aqueous H_2O_2 and lipophilic alkene. Hence, catalyst **1** in conjunction with $[Bpy]BF_4$ and $[Dopy]BF_4$ constituted the amphipathic IL compositions (**ILC**), in which the epoxidation of lipophilic alkenes by aqueous H_2O_2 could occur efficiently in homogeneous phase (Scheme 1). The attractive advantages of alkene epoxidation in the **ILC** could arise from the recyclability of the IL phase together with the embedded catalyst (**1**), as well as the typical IL effects on activity, stability, and/or selectivity promotions.

2. Experimental

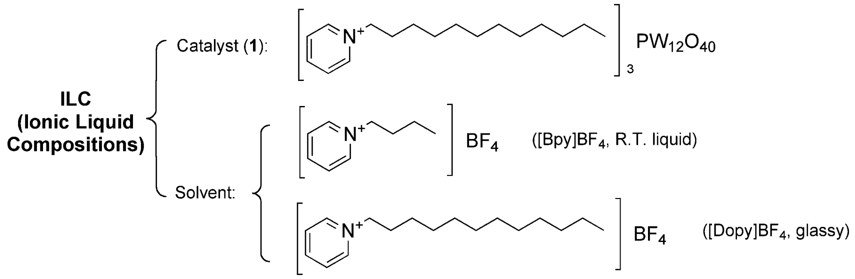
2.1 Reagents and analysis

Keggin-type phosphotungstic acid ($H_3[PW_{12}O_{40}].XH_2O$) and other chemical reagents were purchased and used as received. The IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The ^{31}P NMR spectra (with 85% H_3PO_4 sealed in a capillary tube as internal standard) were recorded on a Bruker Avance 500 spectrometer. The elemental analyses for P and W were performed by an inductive coupled plasma (ICP) emission spectrometer (RIS Intrepid II XSP spectrometer, Thermo Electron Corporation). TG was acquired using a Mettler TGA/SDTA 851^e instrument and STARe thermal analysis data processing system. TG analyses were run in air flow with a temperature ramp of 10 °C min^{-1} between 50~800 °C. The UV-visible spectra were recorded on a SHIMADZU-UV 2550 spectrophotometer with a resolution of *ca.* 1 nm. GC analyses were performed on a SHIMADZU-14B chromatography equipped with Rtx-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-MS analyses were recorded on an Agilent 6890 instrument equipped with Agilent 5973 mass selective detector.

2.2 Synthesis

N-*n*-Dodecylpyridinium phosphotungstate ($[Dopy]_3[PW_{12}O_{40}]$, 1) and N-*n*-butylpyridinium phosphotungstate ($[Bpy]_3[PW_{12}O_{40}]$, 2) with typical Keggin-type structure. The aqueous solution of N-*n*-dodecyl pyridinium bromide ([Dopy]Br) was added dropwise into the aqueous solution of phosphotungstic acid ($H_3[PW_{12}O_{40}].XH_2O$) under vigorous stirring. The white solids were immediately precipitated from the solution. When no precipitates were formed anymore, the white solids were collected and then dried in an oven at 60 °C after thoroughly washing with deionized water, yielding the product of $[Dopy]_3[PW_{12}O_{40}]$ (**1**). The similar procedures were applied to the synthesis of $[Bpy]_3[PW_{12}O_{40}]$ (**2**). TG analysis (in air flow): the thermal decomposition temperature of **1** is *ca.* 340 °C; the thermal decomposition temperature of **2** is *ca.* 360 °C. ^{31}P NMR of **1**: −14.1 (in DMF-d_7). FT-IR of **1** (KBr disc): 3133, 3080, 2929, 2857, 1633 (C=N), 1487 (C=C), 1084 (P-O_a), 982 (terminal W-O_d), 896 (inter-octahedral W-O_b-W), 808 (intra-octahedral W-O_c-W) cm^{-1}. UV-Vis of **1**: 265 nm (in DMF) or 295 nm (in $[Bpy]BF_4$).

N-*n*-Dodecyl pyridinium phosphotungstate ($[Dopy]_4Na_3$-$[PW_{11}O_{39}]$, 3) with lacunary Keggin-type structure. The lacunary phosphotungstate derivative, $[PW_{11}O_{39}]^{7-}$, could be obtained easily from the typical Keggin-type phosphotungstic acid ($H_3[PW_{12}O_{40}].XH_2O$).[26,27] The aqueous solution of phosphotungstic acid ($H_3[PW_{12}O_{40}].XH_2O$) was treated with NaOH aqueous solution to adjust the pH value to 7.5. The obtained solution in pale-blue color was then treated dropwise with the aqueous solution of excess N-*n*-dodecyl pyridinium bromide, along with the rapid formation of the pale-white precipitates. The solids were collected and dried in oven at 60 °C after thoroughly washing with deionized water, yielding the product of $[Dopy]_xNa_{7-x}[PW_{11}O_{39}]$ (x= 1–7, **3**). TG analysis (in air flow): The thermal decomposition temperature of **3** is *ca.* 220 °C. According to 27.7% weight loss of **3** ($[Dopy]_xNa_{7-x}[PW_{11}O_{39}]$) due to the combustion of *n*-dodecyl pyridinium at the range of 220~500 °C (Fig. 1), the value of x in the molecular formula was confirmed to be 4. ^{31}P NMR of **3**: −9.6 ppm (in $[Bpy]BF_4$). ^{31}P NMR of $Na_7[PW_{11}O_{39}]$: −10.3 ppm (in H_2O). FT-IR of **3** (KBr disc): 1084 and 1044 (P-O), 951 (W-O_d), 896 and 854 (bridge W-O_b), 808 and 743 (bridge W-O_b) cm^{-1}.



Scheme 1 The compositions of the amphipathic functionalized ionic liquids

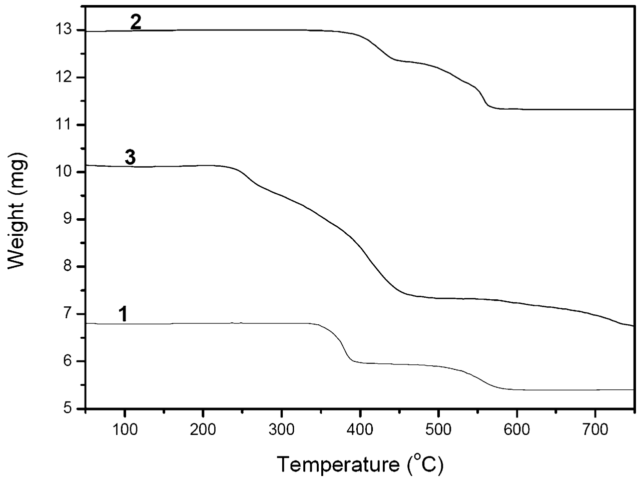


Fig. 1 TG analysis of **1**, **2** and **3** in air flow.

2.3 General procedures for alkene epoxidations catalyzed by 1 in the ILs of [Dopy]BF$_4$-[Bpy]BF$_4$

For the typical experiment, to 1.5 mL [Dopy]BF$_4$ and 1.5 mL [Bpy]BF$_4$ was added *cis*-cyclooctene (5 mmol), 30% H_2O_2 (7.5 mmol), and **1** (1 mol%). The obtained mixtures were stirred vigorously in the sealed glass vials at 80 °C for 1 h on an Advantage Series ™ 2410 Personal Screening Synthesizer (Argonaut Technologies Inc). Upon completion, diethyl ether was used to extract the organic compounds (2 mL × 6). The conversions of the substrates were based on GC analyses with *n*-dodecane as internal standard. The selectivities of the products were based on GC analyses with normalization method. The products were further identified by GC-Mass analysis.

The left IL phase containing water was directly used without further treatment for the next run. In each run, due to the stoichiometric consumption of the oxidant, 30% H_2O_2 was added (7.5 mmol) additionally besides the substrate.

3. Results and discussion

3.1. Characterization of 1–3

[Dopy]Br and $H_3[PW_{12}O_{40}].XH_2O$ are highly soluble in water, but the association of $[PW_{12}O_{40}]^{3-}$ anions with [Dopy]$^+$ leads to the rapid precipitation of insoluble compounds. This behavior guaranteed the desired association of [Dopy]$^+$ cations with $[PW_{12}O_{40}]^{3-}$ anions at the stoichiometric ratio. The TG analysis in Fig. 1 revealed that the stoichiometric ratio of [Dopy]$^+$ to $[PW_{12}O_{40}]^{3-}$ in **1** was 3, which was consistent with 20.6% weight loss at the range of 340~600 °C due to the total loss of *n*-dodecylpyridinium group. The TG analysis for **2** also confirmed the stoichiometric ratio of 3 for [Bpy]$^+$/$[PW_{12}O_{40}]^{3-}$ in **2**, with 12.9% weight loss at the range of 350~600 °C. Similarly, according to 27.7% weight loss of **3** ($[Dopy]_xNa_{7-x}[PW_{11}O_{39}]$) in Fig. 1, the value of x in the molecular formula was confirmed to be 4.

On the other hand, it was found that the typical Keggin-type $[PW_{12}O_{40}]^{3-}$ was very sensitive to the change of the pH value. When the pH value of the aqueous solution increased to *ca.* 5,[26] the typical Keggin-type $[PW_{12}O_{40}]^{3-}$ transformed into the lacunary Keggin-type derivative $[PW_{11}O_{39}]^{7-}$, with the characteristic IR vibrations as shown in Fig. 2 (P-O (1084 and 1044 cm^{-1}), bridge W-O$_b$/$_c$ (896, 854; 808, 743 cm^{-1}), and W-O$_d$ (951 cm^{-1}).[27] Hence, the association of neutral [Dopy]$^+$ cations, instead of basic NH_4^+, K^+ or Na^+, with $[PW_{12}O_{40}]^{3-}$ anions could guarantee the maintenance of the typical Keggin-type structure in the resultant ionic compound **1** (Fig. 2).

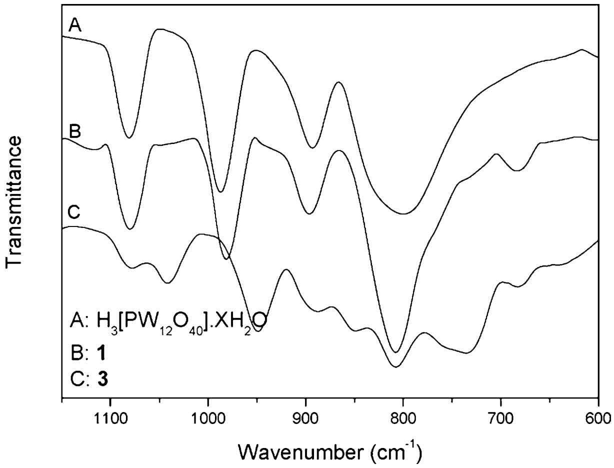


Fig. 2 FT-IR spectra of **1**, **3** and $H_3[PW_{12}O_{40}].XH_2O$.

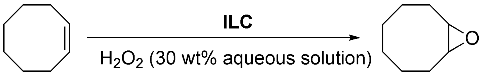
3.2. Epoxidation of *cis*-cyclooctene by H_2O_2

One purpose of this study was to design a totally homogeneous reaction environment suitable for the epoxidation of lipophilic alkenes oxidized by hydrophilic H_2O_2 and catalyzed by the solid phosphotungstate salt, which was expected to be fulfilled through the fabrication of the **ILC**. The epoxidation of *cis*-cyclooctene by commercial 30%H_2O_2 aqueous solution was selected as the model reaction. When *cis*-cyclooctene was mixed with [Bpy]BF$_4$ without the presence of [Dopy]BF$_4$, the biphasic mixture was obtained even under vigorous stirring. When [Dopy]BF$_4$ was used together with [Bpy]BF$_4$ at a volume ratio of 1, *cis*-cyclooctene and H_2O_2 were completely miscible in the IL mixture of [Bpy]BF$_4$ and [Dopy]BF$_4$. It was found that at room temperature **1** was not very soluble in the solution composed of *cis*-cyclooctene (5 mmol), 30% H_2O_2 (7.5 mmol), [Bpy]BF$_4$ (1.5 mL), and [Dopy]BF$_4$ (1.5 mL), but it gradually dissolved at 80 °C when the epoxidation was performed, resulting in a completely homogeneous solution, which maintained invariably after completion and cooling to room temperature (see ESI†).

The key reaction conditions were optimized in details as presented in Table 1 and Table 2. The increased amount of H_2O_2 obviously led to the higher conversion (Entry 8), and the selectivity to the epoxide decreased with the increase of temperature (Entries 1–3). In consideration of the possible negative effect of excess oxidant on the catalyst stability, 7.5 mmol H_2O_2 was used in the following experiments. Under the optimal conditions (80 °C, 1 h, 1 mol% **1**, and H_2O_2 7.5 mmol), 88% conversion was obtained with 95% selectivity to cyclooctane epoxide (Entry 2 in Table 1).

In contrast, when the epoxidation was performed in the polar organic solvent of DMF, the homogeneous solution was obtained immediately after mixing *cis*-cyclooctene, aqueous H_2O_2, and **1** with DMF together. Although no mass transfer limitation

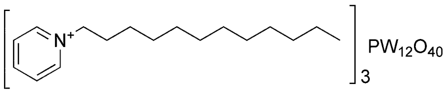
Table 1 Epoxidation of *cis*-cyclooctene catalyzed by the **ILC** under different conditions[a]



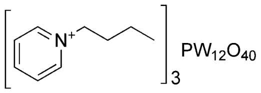
Entry	Temperature (°C)	Concentration of **1** (mol%)	H_2O_2 amount (mmol)	Conversion (%)	Epoxide Selectivity (%)[b]
1	70	1	7.5	81	99
2	80	1	7.5	88	95
3	90	1	7.5	90	92
4	80	0.5	7.5	76	95
5	80	1.5	7.5	89	95
6	80	1.0	2.5	31	95
7	80	1.0	5	58	96
8	80	1.0	10	99	96

[a] *Cis*-cyclooctene 5 mmol, $[Bpy]BF_4$ 1.5 mL, $[Dopy]BF_4$ 1.5 mL, reaction time 1 h; [b] The trace hydrolyzed products from epoxide and the cleaved products were found, which were confirmed by GC-Mass analysis.

Table 2 Epoxidation of *cis*-cyclooctene catalyzed by **1–3** in the ILs or DMF[a]



1



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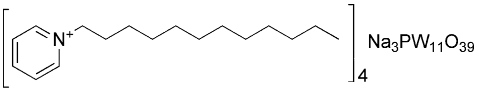

3

Entry	Catalyst	Solvent	Conversion (%)	Epoxide selectivity (%)[e]
1[b]	**1**	ILs	88	95
2[c]	**1**	DMF	69	100
3[b,d]	Used **1**	ILs	60	100
4[b,d]	Used **1**	DMF	74	96
5[b]	**2**	ILs	83	96
6[c]	**2**	DMF	61	100
7[b]	**3**	ILs	71	95

[a] Catalyst 0.05 mmol (1 mol%), *cis*-cyclooctene 5 mmol, 30 wt% H_2O_2 7.5 mmol, temperature 80 °C, reaction time 1 h, ILs $[Bpy]BF_4$ (1.5 mL)-$[Dopy]BF_4$ (1.5 mL), DMF 3 mL. [b] The liquid (*cis*-cyclooctene, ILs, H_2O_2)-solid (catalyst) biphasic system after mixing, which gradually changed to a homogeneous one during epoxidation. [c] The homogeneous system from the beginning to the end. [d] Used **1** was the solid precipitated from the reaction mixture in Entry 1 after quenching by ethanol at 80 °C upon completion immediately. [e] The hydrolyzed products from the epoxide and the cleaved products were found, which were confirmed by GC-Mass analysis.

occurred in such case, the conversion of *cis*-cyclooctene was relatively lower (Entries 2 *vs.* 1 in Table 2), suggesting the synergetic effect of the ILs of $[Dopy]BF_4$-$[Bpy]BF_4$ on the activity promotion of **1**. Comparatively, **1** with $[Dopy]^+$ cations obviously exhibited the better activity than **2** (Entries 1 and 2 *vs.* 5 and 6), assumingly due to the more available accessibility of the lipophilic substrate to **1** featured with lipophilic dodecyl tail. **3** with the lacunary Keggin-type structure showed relatively lower activity than **1**, which was consistent to the work reported before.[28]

Table 3 Recycling use of the **ILC** for *cis*-cyclooctene epoxidation[a]

Run	H_2O was accumulated		H_2O was removed in each run	
	Conversion (%)	Epoxide selectivity (%)[b]	Conversion (%)	Epoxide selectivity (%)[b]
1	88	95	89	95
2	90	100	90	100
3	88	100	90	99
4	84[c]	99	90	99
5	85	100	91	98
6	84	99	90	99

[a] **1** 0.05 mmol (1 mol%), *cis*-cyclooctene 5 mmol, 30% wt H_2O_2 7.5 mmol, temperature 80 °C, reaction time 1 h, $[Bpy]BF_4$ (1.5 mL)-$[Dopy]BF_4$ (1.5 mL). [b] The trace hydrolyzed products from epoxide and the cleaved products were found, which were confirmed by GC-Mass analysis. [c] The upper accumulated aqueous phase was removed by decantation, and then 0.5 mL $[Bpy]BF_4$ and 0.5 mL $[Dopy]BF_4$ were additionally added.

The request for easily separable and recyclable catalysts is driven by economic consideration and environmental concerns. Along this issue, the recovery and recyclability of the **ILC** were investigated in Table 3. Upon completion in each run, the clear reaction solution was cooled to room temperature. The substrate and the products were extracted with diethyl ether for GC and GC-Mass analyses. The left IL phase containing byproduct H_2O was used directly without further treatment. It was found the accumulated H_2O during the recycling showed no negative effect on the activity of **1**. However, with the accumulation of H_2O in the **ILC**, the biphasic system was obtained after the 4th run, and the catalyst was partially precipitated from the IL phase. Hence, after extraction by diethyl ether for GC analysis, the upper aqueous phase was removed by decantation. The left IL phase was further used for next runs after refilling 0.5 mL $[Bpy]BF_4$ and 0.5 mL $[Dopy]BF_4$, leading to the conversions of 85% in

5th run and 84% in 6th run, respectively. The ICP analysis for W element indicated that the loss of **1** in the combined organic phase and the removed aqueous phase was less than 0.1%. The final obtained **ILC** phase containing some accumulated H_2O_2 after 6 runs showed a single peat at −14.7 ppm in ^{31}P NMR spectra (Fig. 3-C), which was nearly the same as that for the fresh **1** (Fig. 3-A, −14.1 ppm), indicating the intactness of catalysts **1** after the epoxidation without any observable degradation and decomposition. However, if the reaction mixture after the 1st use (Entry 1 in Table 2) was quenched at 80 °C immediately with ethanol to precipitate the solid catalyst (referred to as used **1**), the lower activities of which were observed in the following reuse no matter in the ILs or DMF (Entries 3 and 4 in Table 2). It was found that the IR spectrum of used **1** (1081 and 1042 (P-O), 950 (W-O_d), 895 and 850 (bridge W-O_b), 810 and 745 (bridge W-O_b) cm^{-1}) was nearly the same as that of **3** in Fig. 2-C, and that its ^{31}P NMR spectrum (Fig. 3-B) showed two signals at −8.6 and −9.5 ppm, indicating that the lacunary Keggin heteropolyanion $[PW_{11}O_{39}]^{7-}$ was formed when the used **ILC** was quenched by cool ethanol at 80 °C. Although the signal at −8.6 ppm was unable to be assigned concisely, it was believed to correspond to a kind of depolymerized phosphotungstate derivative also with the lacunary Keggin structure.[27,29] These results suggested that, with involvement of H_2O_2, the pre-catalyst **1** convert to the active peroxo-species in charge of oxygen transfer and substrate activation,[12–14] which could reversibly return to **1** with the presence of the ILs, otherwise the formed peroxo-species depolymerize to the lacunary Keggin-type derivatives like $[PW_{11}O_{39}]^{7-}$ *etc.* when the IL surroundings were unavailable.

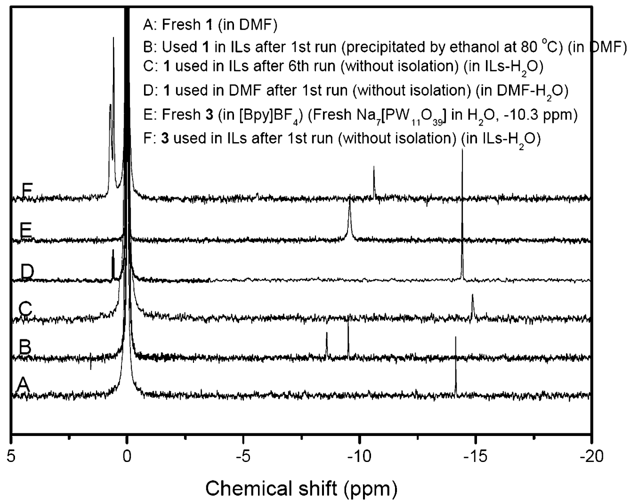

Fig. 3 The ^{31}P NMR spectra of the fresh and the used catalysts.

On the other hand, if the formed byproduct of water was removed at 90 °C upon completion in each run, the activity of the **ILC** maintained even better. After six runs, no activity loss was observed as shown in Table 3. The ^{31}P NMR analysis of the reaction solution in each run also indicated that **1** retained as intact as the fresh one after the recycling (δ=-14.1 ppm).

Comparatively, with DMF as the solvent, the used solution in Entry 2 of Table 2 presented two the peaks at 0.6 and −14.5 ppm (Fig. 3-D). The appearance of 0.6 ppm signal was attributed to the formation of depolymerized P-containing species, which indicated the slight degradation of **1** in DMF with the presence of H_2O_2.[13,14,29]

As for **3** used in the ILs for the epoxidation (Entry 7 of Table 2), the ^{31}P NMR spectra indicated that two strong signals at 0.7 and 0.6 ppm, which were also ascribed to the P-containing species derived from the degradation of **3**, besides the one at −10.5 ppm ascribed to the original lacunary Keggin-type $[PW_{11}O_{39}]^{7-}$ of **3** (Fig. 3-F).

Hence, it was indicated that the relatively lower activity of **1** in DMF or **3** in the ILs resulted from the degradation of the corresponding catalyst, whereas the **ILC** system went through the epoxidations for 6 runs, the degradation of **1** was unobservable completely.

3.2. The generality of the ILC towards alkene epoxidations

The generality of the **ILC** to the different alkenes was investigated in Table 4, in which cycloalkenes, long-chain alkenes, and styrene derivatives were selected. It was found that with H_2O_2 as oxidant, the selectivities to the corresponding epoxides were dramatically decreased due to the formation of the hydrolyzed products from epoxides and the cleaved products. Hence, the reaction temperature was decreased to 70 °C to suppress the pass-ways to the side-products. As shown in Table 4, with the cycloalkenes and styrene derivatives, the **ILC** exhibited moderate to good activity but relatively lower selectivities to

Table 4 Epoxidations of the different alkenes in the **ILC** oxidized by H_2O_2 or UHP[a]

		H_2O_2 as oxidant		UHP as oxidant	
Entry	Alkene	Conversion (%)	Epoxide selectivity (%)[b]	Conversion (%)	Epoxide selectivity (%)[b]
1	*Cis*-cyclooctene	88	98	97	99
2	Cyclohexene	80	56	90	57
3	Norbornene	76	34	91	87
4	Styrene	66	29	63	29
5	4-Chlorostyrene	49	46	56	86
6	4-Bromostyrene	44	52	53	89
7	4-Methylstyrene	63	10	77	24
8	Ethyl cinnamate	< 5	—	< 5	—
9	1-Octene	10	21	22	100
10	1-Dodecene	7	30	8	98

[a] **1** 0.05 mmol (1 mol%), alkene 5 mmol, 30% H_2O_2 7.5 mmol, ILs [Dopy]BF_4 (1.5 mL)-[Bpy]BF_4 (1.5 mL), reaction temperature 70 °C, reaction time 2 h. [b] The hydrolyzed products from the epoxide, the cleaved products, and/or the double-bond-shift products were found, which were confirmed by GC-Mass analysis.

epoxides in comparison to the case of *cis*-cyclooctene. For cyclohexene, besides the targeted cyclohexane epoxide, adipic acid was found in high selectivity (*ca.* 30%, Entry 2). In cases of styrene derivatives, the presence of electron-withdrawing groups (–Cl, –Br) seemingly favored the epoxide selectivities (Entries 5 and 6). The increased electron-density at α-C of the side chain in 4-methylstyrene led to increased selectivity to the oxidative cleavage products of 4-methylbenzaldehyde and 4-methylbenzoic acid (Entry 7). However, for ethyl cinnamate with internal C=C bond, the conversion of this substrate was nearly non-detectable, probably due to the facial non-access of the internal C=C bond to the active site of catalyst **1** (Entry 8). As for the long-chain alkenes like 1-octene and 1-dodecene, the activation of such alkenes were still difficult to fulfill in the **ILC**, due to the propensity to the formation of the cleaved byproducts and double-bond-shift byproducts. It was also found that, when urea hydrogen peroxide (UHP) was in place of H_2O_2 aqueous solution as the oxidant, the selectivities to epoxides in Entries 2–7 were dramatically improved with the comparative or better conversions of the corresponding alkenes (Entries 3, 5, 6, 7, 9, and 10). Especially for norbornene, 91% conversion and 87% selectivity to norbornane epoxide were obtained by using UHP as the oxidant; for 1-octene and 1-docecene, the double-bond-shift byproducts and the cleaved byproducts were nearly unobservable, although the conversions were still relatively low.

Conclusions

In this work, the homogenization of H_2O_2-based POM-catalyzed lipophilic-alkene epoxidation was realized through the fabrication of the **ILC**, which guaranteed the high efficiency of homogeneous catalysis and the available recovery/recyclability of the solvent-catalyst system as the merit of heterogeneous catalysis. The constructed **ILC** exhibited the improved catalytic behaviors in terms of activity, stability and recyclability with typical characteristics of ILs. In which the ILs of [Bpy]BF_4-[Dopy]BF_4 not only acted as the amphipathic solvent to provide a homogeneous reaction environment for hydrophilic H_2O_2 oxidant, lipophilic alkene, and solid POM catalyst **1** with typical Keggin-type structure, but also protected catalyst **1** from oxidative degradation. Under the similar conditions, however, catalyst **3** with the lacunary Keggin-type structure proved to be more susceptible to the oxidative destruction than **1** in the course of epoxidation.

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