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Peroxopolyoxometalate-based room temperature ionic liquid as a self-separation catalyst for epoxidation of olefins

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ABSTRACT

A new peroxopolyoxometalate-based room temperature ionic liquid (POM-RTIL) has been synthesized and used as catalyst for efficient epoxidation of various olefins. The RTIL catalyst was found to be well dissolved in the solvent (ethyl acetate) during the reaction, while it can self-separate from the reaction media at room temperature after the reaction completed, which made the recovery and reuse of the IL catalyst convenient. The POM-RTIL catalyst can be recycled for five times without significant loss of activity.

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1. Introduction

Epoxidation of olefins is an important reaction in laboratory as well as in the chemical industry, because epoxides are widely used for manufacturing epoxy resins, surfactants, and intermediates, etc. in organic synthesis [1]. H_2O_2 -based catalytic epoxidation has received much attention from an economic and environmental point of view [2]. It has been known that the tungsten-based catalysts like polyoxometalate (POM) show high efficiency of hydrogen peroxide utilization and high selectivity towards epoxides [3,4]. Among different polyoxometalates, the classic Ishii-Venturello system [5,6] has attracted huge interests and has been investigated extensively by different groups. The Venturello anion ($\{PO_4[WO(O_2)_2]_4\}^{3-}$) was found to be the most important active species in Ishii-Venturello system [7–11].

As a highly active oxidation species, Venturello anion was combined with quaternary ammonium in conjunction with H_2O_2 as primary oxidant for epoxidation of various olefins under mild conditions [6,12,13]. Venturello anion has also been immobilized on macroreticular Amberlite IRA-900 (exchange resin) [14], silicate xerogel [15] and dendrimer [16–18] to facilitate the recycling of catalyst. When coupled with 1-butyl-3-methylimidazolium cation, the Venturello anion can be immobilized in ionic liquid for the oxidation of secondary alcohols [19].

Room temperature ionic liquids (RTILs) are ionic liquids (ILs) that are liquid at room temperature or slightly higher (20–30 °C). RTILs as

successful alternative solvents for homogeneous biphasic catalysis have been designed for immobilizing catalysts, facilitating product isolation and recycling the catalyst. The first POM-based RTIL was reported by Bourlinos et al. [20]. In their communication they showed the possibility to yield a liquid derivative of POM by partial exchange of the protons of the POM with a PEG-containing quaternary ammonium. This new IL showed similar properties compared with other conventional ILs, such as low melting point, comparable viscosity and thermal stability. Then Rickert et al. reported that the combination of a Keggin or Lindqvist anion with tetraalkylphosphonium cation can also yield POM-RTILs [21,22]. Though many Venturello anion-based catalytic systems have been reported, as far as we know, no Venturello anion-based RTIL is known and utilized in catalysis yet.

In this work, we present two novel POM-RTILs prepared by pairing alkylimidazolium cation with the well-defined Venturello anion. The RTILs were highly active for the epoxidation of various olefins and proved to be self-separation catalysts, which led to easy separation of the products from the IL catalysts *via* simple decantation.

2. Experimental

2.1. General remarks

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. All solvents (A.R. grade) were dried with the standard





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methods. Triethylamine, *N*-butylimidazole and thionyl chloride (Sinopharm Chemical Reagent Co., Ltd, Shanghai, A.R. grade) were distilled and PEG-300 was dried at 60 °C under vacuum for 4 h prior to use. Imidazole (Sinopharm Chemical Reagent Co., Ltd, Shanghai, A.R. grade) was used as received without further purification. All NMR spectra were recorded on a Bruker Avance 500 instrument (500 MHz ¹H) using CDCl₃ and TMS as solvent and reference, respectively. Chemical shifts (δ) were given in parts per million and coupling constants (*J*) in Hertz. The products were analyzed by GC and GC–MS equipped with a HP-5MS column (30 m long, 0.25 mm i.d.).

2.2. Synthesis of ionic liquid catalyst (5a, 5b)

The synthesis of the ionic liquid catalyst was shown in Fig. 1. 5b was taken as an example. Firstly, *N*-dodecylimidazole (3b, ¹H-NMR (500 MHz, CDCl₃) δ = 7.45(s, 1H, CH), 7.02(s, 1H, CH), 6.88(s, 1H, CH), 3.90(t, 2H, CH₂), 1.74(m, 2H, CH₂), 1.27(m, 18H, CH₂), 0.86(t, 3H, CH₃)) and PEG dichlorides (IR cm⁻¹: 2880, 1963, 1672, 1468, 1279, 1113, 946, 842, 745, 665(C–Cl), 531) were synthesized according to the previously reported procedures, respectively [23,24].

The PEG chain-functionalized *N*-dodecylimidazolium dichlorides (4b) were synthesized by the following steps. 1.5 mmol chlorinated PEG-300 and 4 mmol 3b were charged into a steel vessel, and allowed to react at 90 °C for 48 h under 1.0 MPa nitrogen with magnetically stirring. Then the product (4b) was washed with diethyl ether for four times and treated under vacuum to give the product. ¹H-NMR (500 MHz, CDCl₃) δ = 10.68(s, 2H, CH), 7.64(s, 2H, CH), 7.18(s, 2H, CH), 4.60(t, 4H, CH₂), 4.21(t, 4H, CH₂), 3.30-3.80(m, PEG), 1.75(m, 4H, CH₂), 1.28(m, 36H, CH₂), 0.86(t, 6H, CH₃). ¹³C NMR(125 MHz, CDCl₃) 136.7, 123.3, 121.6, 70.2-69.9, 68.8, 65.5, 49.6, 29.2, 14.9, 13.8.

Correspondingly, the ionic liquid catalyst (5b) was prepared conveniently according to the following steps. After the solution of H₃PW₁₂O₄₀ (1.6 g, 0.6 mmol) in 12 ml of 30% H₂O₂ was stirred for 30 min, 4b (0.7 g, 0.9 mmol) in 10 ml of dichloromethane was added dropwise. The resulting biphasic mixture was thoroughly stirred for another 30 min. Then the organic layer was separated and dried under anhydrous air flow at 40 °C for 4 h to give an almost colorless transparent viscous ionic liquid catalyst (5b). IR (cm⁻¹): 3141, 3106, 2924 and 2854 (CH); 1736 and 1563 (CC and CN); 1465 and 1350 (CH); 1162 and 1105 (CO); 844 (OO); 523 (WOO) (Fig. 2). The bands resulted from P–O and W=O were overlapped by the characteristic bands of PEG chain ranged from 900 to 1200 cm⁻¹. As shown in Fig. 3, ³¹P NMR (CDCl₃) of IL 5b gave mainly five signals at different chemical shift ranged from -10 to 10 ppm, which were ascribed to the "aged" Venturello anion since it was very liable to change. This phenomenon was found by Hill's group [11] in the in-depth study of the Venturello complex and also observed by Kozhevnikov's group [13] in the epoxidation of oleic acid catalyzed by $Q_3\{PO_4[WO(O_2)_2]_4\}$ (Q = quaternary ammonium).

2.3. Typical procedure for epoxidation of cyclooctene by using RTIL catalysts

For the reaction in the absence of solvent, IL catalyst (50 mg) was charged into a 50 ml steel vessel, followed by adding 3 mmol H_2O_2 and 3 mmol cyclooctene. Then the vessel was heated to the required temperature with magnetically stirring for a certain time. After the reaction, the product was extracted with cyclohexane for



Fig. 1. Typical preparation procedure of the ionic liquid catalysts (5a, 5b). Reagents and conditions: (a) Triethylamine, CH₂Cl₂, 0 °C, 24 h. (b) DMF, NaH. (c) Benzene, pyridine, reflux, 10 h. (d) 90 °C, 48 h. (e) CH₂Cl₂, H₂O₂.



3 times for the GC analysis. The catalyst remained in the steel vessel was treated under vacuum at 60°C for 2 h, and then reused for the next cycle.

For the reaction in the presence of organic solvent (5 ml), the similar procedure was adopted except that 3 ml cyclohexane was added to the reaction mixture to facilitate the catalyst separation after the reaction. Then solvent phase was removed, and the catalyst was washed with cyclohexane and further treated under vacuum for the next run.

3. Results and discussion

Fig. 1 showed the synthetic route of the ionic liquid catalysts (5a and 5b). The reaction of *N*-dodecylimidazole with PEG dichlorides afforded dicationic dichlorides bridged by polyether linkage chains (4b) in high yield. Venturello anion was obtained by the degradation of $H_3PW_{12}O_{40}$ in excess of H_2O_2 [11]. Then the IL 5b was obtained by ion-exchange in aqueous-organic biphasic system

(Fig. 1). When the PEG functionalized *N*-hexyl imidazolium dichlorides (4a) were used instead of 4b, Venturello anion-based RTIL (5a) can also be separated from the organic layer. But the PEG chain functionalized *N*-butyl imidazolium dichlorides were proved to be too hydrophilic to transfer the Venturello anion into the organic phase. Accordingly, no Venturello anion-based RTIL was obtained when organic solvent was removed.

The ILs 5a and 5b were first employed to epoxidize cyclooctene in the absence of solvent. As shown in Table 1, IL catalyst 5a with a shorter alkyl chain showed lower activity than that of 5b at 20 °C (Entries 1 and 2, Table 1). But at 60 °C, a nearly full conversion of cyclooctene was achieved by using both of catalysts after 4 h (Entries 3 and 4, Table 1). The reaction was obviously accelerated at higher temperature (Entries 1 and 3, Table 1). Because the IL catalysts (5a, 5b) were immiscible with cyclohexane, the extraction of products and the separation of IL catalyst were achieved conveniently by adding cyclohexane. After extraction, the catalyst was treated under vacuum for the next run. It can be reused for another four times without obvious loss of activity (Entries 4–8, Table 1).

Table 1			
Epoxidation	of olefins	without	solvent. ^a

Entry	Substrates	IL catalyst	Temperature (°C)	Concentration (%)	Selectivity (%)
1	Cyclooctene	5a	20	25	99
2	Cyclooctene	5b	20	60	99
3	Cyclooctene	5a	60	96	99
4	cyclooctene	5b	60	95	99
5	2nd Run	5b	60	91	99
6	3rd Run	5b	60	92	99
7	4th Run	5b	60	90	99
8	5th Run	5b	60	89	99
9	Styrene	5b	60	94	86 ^b
10	Cyclohexene	5b	60	89	23 ^c

^a Fifty milligram IL catalyst, 3 mmol substrate, 3 mmol H₂O₂ Reaction time: 4 h. ^b The main products were benzyl aldehyde and benzoic acid. The selectivity to styrene oxide was less than 2%.

^c The 1,2-cyclohexanediol and 2-hydroxy cyclohexanone were detected as main by-products.

When styrene or cyclohexene was used as substrate in the absence of solvent, although high conversions were achieved in both cases, the selectivities to the epoxide were always poor due to the acidic hydrolysis of the epoxide ring by direct contact with the acid aqueous phase where acidity likely resulted from the degradation of the anion [13] (Entries 9 and 10, Table 1).

In a conventional Ishii-Venturello system, an organic phase is always introduced into the reaction system to protect the epoxides

Table 2

Epoxidation of olefins by using IL 5b in different organic solvents.^a

from the acidic hydrolysis of the epoxide ring. Although chlorocarbons have been widely used as reaction media for the epoxidation, their high toxicity largely defeated the environmental advantages of using the green oxidant H_2O_2 Therefore, the application of environmentally benign solvents in epoxidation would be highly requirable. As a result, several different organic solvents have been screened by choosing the epoxidation of cyclooctene as a model reaction. As shown in Table 2, the cyclooctene was transformed into the corresponding epoxide efficiently in most selected organic solvents (Entries 1–3, Table 2). The lowest activity was obtained with cyclohexane as reaction media (Entry 4, Table 2), which can be explained by the negligible solubility of IL 5b in nonpolar cyclohexane. Because ethyl acetate is a low toxic solvent, it was sequentially chosen as reaction media for all the reactions.

Although the molar ratio of substrate to H_2O_2 had little influence on the selectivity of cyclooctene epoxidation (Entries 3 and 5, Table 2), it affected that of cyclohexene significantly. When the molar ratio of substrate to H_2O_2 was kept at 3:1, the oxidation of cyclohexene can afford epoxide in high selectivity (97%). However, the selectivity to cyclohexene oxide decreased to 75% when the molar ratio of substrate to H_2O_2 was lower (1:1) (Entries 6 and 7, Table 2).

In the next step, we examined the reaction kinetics over catalysts 5a and 5b in ethyl acetate. The time profile of cyclooctene conversion is given in Fig. 4, which showed that catalyst 5b with a longer alkyl chain was more efficient than catalyst 5a. According to the mechanism proposed by Ishii [25], in the epoxidation of ole-

Entry	Substrates	Substrate/H ₂ O ₂ (molar ratio)	Solvents	Concentration (%)	Selectivity (%)
1	Cyclooctene	3:1	Dichloromethane	98	99
2	Cyclooctene	3:1	Benzene	96	99
3	Cyclooctene	3:1	Ethyl acetate	97	99
4	Cyclooctene	3:1	Cyclohexane	45	99
5	Cyclooctene	1:1	Ethyl acetate	91	99
6	Cyclohexene	3:1	Ethyl acetate	90	97
7	Cyclohexene	1:1	Ethyl acetate	86	75

^a Fifty milligram IL 5b, 3 mmol substrate, 5 ml solvent. Reaction conditions: 60 °C, 4 h. Conversion based on the H_2O_2 charged.



Fig. 4. Time profile of epoxidation of cyclooctene catalyzed by IL catalysts 5a and 5b. Reaction conditions: 50 mg IL, 3 mmol cyclooctene, 1 mmol H₂O₂, 5 ml ethyl acetate, 60°C. The selectivity to cyclooctene oxide was always over 99%.

Table 3			
Epoxidation of various	olefins by using	g catalyst 5a	and 5b. ^a

Entry	Substrate	Catalyst	Temperature (°C)	Time (h)	Concentration ^b (%)	Selectivity (%)
1	Cyclooctene	5b	60	4	97	99
2	2nd Run	5b	60	4	97	99
3	3rd Run	5b	60	4	96	99
4	4th Run	5b	60	4	91	99
5	5th Run	5b	60	4	92	99
6	Styrene	5a	60	4	45	77 ^c
7	Styrene	5b	60	4	93	92
8	Cyclohexene	5a	60	4	42	85 ^d
9	Cyclohexene	5b	60	4	90	97
10	1-Hexene	5a	70	6	30	97
11	1-Hexene	5b	70	6	87	98
12	Geraniol	5b	40	4	85	74 ^e

^a Fifty milligram IL, 3 mmol substrate, 1 mmol H₂O₂, 5 ml ethyl acetate.

^b Conversion based on the H₂O₂ charged.

^c The benzaldehyde and 1-phenyl-1,2-ethanediol were detected as main byproducts.

^d The cyclohexanediol and 2-hydroxy cyclohexanone were detected as main byproducts.

^e Selectivity to 2,3-epoxy alcohol.

fins involving a phase transfer reagent and $PW_{12}O_{40}^{-3}$, the formed peroxo species needed to be transferred into the organic phase (ethyl acetate in our case) where the reaction took place. The more hydrophobic 5b can transfer the active species to the organic phase more efficiently and then gave higher catalytic activity.

The scope of the substrates was also examined. As shown in Table 3, styrene, cyclohexene, 1-hexene and an allylic alcohol (geraniol) were all converted into the corresponding epoxides efficiently by using IL 5b in the H_2O_2 /ethyl acetate system (Entries 7, 9, 11 and 12, Table 3). 5a was found to be much less active than 5b (Entries 6 *vs* 7; 8 *vs* 9; 10 *vs* 11, Table 3). Furthermore, lower selectivity to epoxide was always obtained by using the IL catalyst with shorter alkyl chain IL (5a). This can be explained by the fact that more hydrophilic 5a was more distributed in aqueous phase and then resulted in the further hydrolysis of epoxide product in acidic aqueous phase during the reaction. As a result, the length of alkyl chains attached to imidazolium cation affected not only the activity but also the selectivity.

IL catalyst 5b was immiscible with cyclohexane and water, and the solubility of IL 5b in ethyl acetate was found to be less than 1% at room temperature. However, when 1 mmol of H₂O₂ was added, 5b (50 mg) can be dissolved well in ethyl acetate phase (5 ml) at elevated temperature (40–60 °C). At the end of the reaction, when the mixture continued on cooling to room temperature, most of IL 5b sank to the bottom of the vessel and leaching of the ionic liquid into ethyl acetate was very low. Moreover, the addition of cyclohexane to the reaction solution allowed IL 5b to separate further from organic phase more rapidly. The above observation offered an effective approach to separate the catalyst easily by adding cyclohexane at room temperature after reaction. As shown in Table 3, IL 5b can be employed as self-separable catalyst for five consecutive catalytic cycles in the epoxidation of cyclooctene with a slight decrease in conversion from 97% to 92% (Entries 1-5, Table 3), which might be indicative of the slight deactivation of the recovered catalyst.

Although the precise self-separation mechanism of this new peroxopolyoxometalate-based RTIL was not very clear at this stage, the preliminary experimental results showed that the RTILs as novel environmentally friendly and recyclable catalysts were not only possible but also quite satisfactory.

4. Conclusion

In summary, the first example of epoxidation of olefins catalyzed by a POM-based RTIL was reported here. Various olefins were transformed to epoxides efficiently with high selectivity using a relatively low toxic ethyl acetate as reaction media. The RTIL can be regarded as a self-separation catalyst and reused for five times without significant loss of activity. It is certain that many more catalytically active POM-based RTILs need to be identified. The efforts to explore them are underway in our laboratory.

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