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REGULAR ARTICLE

Investigation of physicochemical properties for novel perrhenate ionic liquid and its catalytic application towards epoxidation of olefins

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Abstract. A novel ionic liquid (IL) based on catalytic functional metal rhenium, [Smim][ReO_4] (1-heptyl-3-methyl-imidazolium perrhenate) was synthesized and characterized. Density and surface tension values of the IL were determined at different temperatures, and the volume and surface properties were calculated and discussed, respectively. Furthermore, the synthesized ionic liquid [Smim][ReO_4] was used as a green solvent and catalyst for homogeneous catalyzed epoxidation of olefin with urea hydrogen peroxide (UHP) oxidant. The effect of factors of catalyst, oxidant, reaction time, and reaction temperature was discussed. The conversion of cyclohexene and cyclooctene is over 99% at optimum conditions. The IL [Smim][ReO_4] as catalyst and solvent are characterized by high efficiency, long service life and recoverability, which is a better green homogeneous catalyst for epoxidation of olefins.

Keywords. Perrhenate ionic liquid; density; surface tension; homogeneous catalysis.

1. Introduction

Ionic liquids (ILs) have attracted attention in research owing to their special characters such as non-volatile, high thermal stability, designable structure, environmentally friendly, recoverable, and exhibit good dissolving ability for many inorganic and organic substances.[1–5] The introduction of structural functionalities on the cationic or anionic part has made it possible to design 'task-specific ILs' with targeted properties.[6] Recently, ILs use in increasingly diverse applications such as fuel cells,[7,8] plasticizers,[9] lubricants,[10] ionogels,[11] extractants[12] and catalysts,[13] etc.

Ecological concerns have given rise to extensive academic research,[14] and the introduction of ILs in industrial applications is well underway.[5] The properties and interactions with other species of ILs such as molecular species or metal complexes to better play their specific role in catalysis. Especially, the contribution ILs make to homogeneous catalysis has more to do with the enhancement of catalytic performances and the possibility of catalyst separation and recycling by immobilization in the IL-phase than with environmental concerns.

Epoxidation of olefins stands out as a crucial class of reactions and is of great interest in academic research and industry due to the production of various important fine chemicals and intermediates.[15–20] The hydrogen peroxide[21–24] and molybdenum-based compounds[25–27] are commonly used as catalysts for epoxidation processes. Along with the continuously study, the researchers found that the polyoxometalate could epoxidize olefins with aqueous hydrogen peroxide at a much more rapid rate in ionic liquids than that in classical organic solvents.[28,29] Rhenium containing compounds have the potential to catalyze the epoxidation of olefins with high efficiency,[30–33] particularly methyltrioxorhenium(VII) (MTO).[34] Meanwhile, ILs as catalyst have also proved to be versatile in oxidation reactions, especially epoxidation of olefins,[35] so the researchers have been introduced the nucleophilic anions into imidazolium salts.[36–38]

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To take advantage of the excellent properties of rhenium catalyst and ILs, we design and synthesis the novel IL-containing catalytic functional metal, which is stable to water and air, then the physicochemical of [Smim][ReO_4] and its catalytic properties were studied.

2. Experimental

2.1 *Materials*

N-methylimidazole (RG) was purchased Suzhou Meihua Daily Chemical Co., Ltd. (Jiangsu, China). Ammonium perrhenate (RG) was bought Hunan rhenium alloy material Co., Ltd. (Hunan, China). 1-Bromoheptane (RG), ethyl acetate (AR), sodium hydroxide (AR), urea hydrogen peroxide (RG), cyclohexene (RG), cyclooctene (RG), epoxy cyclohexane (RG), Karl Fischer reagents without pyridine (AR) and epoxy cyclooctane (GC) were purchased Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water was prepared by multiple distillations.

2.2 *Preparation and characterization of the ionic liquid*

Scheme 1 is a schematic of this synthetic route. According to the literature,[39,40] a slight excess of 1-Bromoheptane was added dropwise to the *N*-methylimidazole, and the mixed solution was stirred under cooling for 24 h at 70 °C. Then, the mixture was washed by the mixture of ethyl acetate and acetonitrile for 3 times and evaporated under reduced pressure at 80 °C. The precursor of 1-heptyl-3-methyl-imidazolium bromide [Smim]Br was prepared and the yield of dark brown viscous liquid was approximately 85%. Then, [Smim]Br and 1.2 equivalent of ammonium perrhenate (NH_4ReO_4) were added to acetone under nitrogen and stirred at indoor temperature for 48 h. The NH_4Br constantly precipitated as the reaction proceeds, which is insoluble in acetone. The slurry was then filtrated by a Büchner funnel, and NH_4Br and residual NH_4ReO_4 were removed. Finally, the IL was obtained by removal of acetone, recrystallizing three times with acetonitrile and ethyl acetate mixed solution, and then dried under vacuum for 24 h. The final product is yellow ionic liquid [Smim][ReO_4].

Structure of the [Smim][ReO_4] was confirmed by ^{1}H-NMR spectroscopy, elemental analysis, differential scanning calorimetry (DSC) and Raman spectra (see the Supplementary Information), respectively. ^{1}H-NMR ($CDCl_3$, 300 MHz, 298 K): $\delta = 8.855$ (s, 1H, -NC*H*N-), 7.373-7.419 (d, 2H, -NC*H* = C*H*N-), 4.229 (t, 2H, -NCH_2CH$_2$-), 4.022 (s, 3H, -NCH_3), 1.921 (m, 2H, -NCH$_2$CH_2CH$_2$-), 1.315 (m, 8H, -NCH$_2$CH$_2$-CH_2CH_2CH_2CH_2CH$_3$), 0.878 ppm (t, 3H, -CH$_2$CH_3). Anal. Calcd for C11H22N2ReO4: C, 30.55; H, 5.10; N, 6.48. The data of DSC showed that [Smim][ReO_4] had no melting point, the glass transition temperature (T_g) was – 69.4 °C. The Raman characteristic peaks of ReO_4^- in [Smim][ReO_4] were 332.68 cm^{-1} and 962.04 cm^{-1}, which were consistent with the reference values of 331 cm^{-1} and 971 cm^{-1}.[15] The water content of the [Smim][ReO_4] is 500 ppm, which was determined by a Karl Fischer moisture titrator (ZSD-2 type).

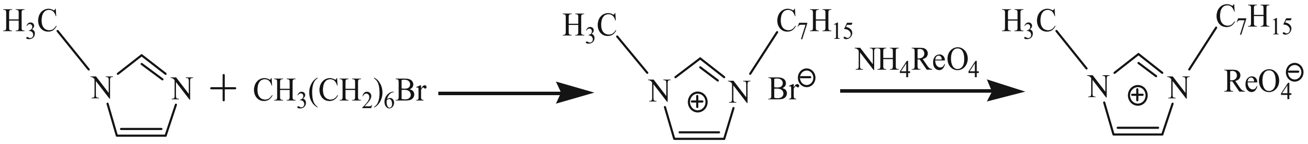
2.3 *Measurement of density and surface tension*

The density of the ultrapure water was measured by a Westphal balance in a temperature range from (293.15 ± 0.01) to (343.15 ± 0.01) K. The results were in good agreement with the literature values,[41] and then the density of the [Smim][ReO_4] was measured by the same method within the experimental error ± 0.0002 g·cm^{-3}.

By use of the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of the sample was measured in the corresponding temperature range as the density, which is within 0.1 mJ·m^{-2} from the literature value.[41]

2.4 *Establishment of a catalytic system*

Generally, the oxidant H_2O_2 was used in the epoxidation of olefins, however, the presence of free



Scheme 1. Schematic of the synthesis for ionic liquid [Smim][ReO_4].

hydrogen ions H^+ in the system caused the epoxy compound to ring-open to produce diol, which led to the decrease of the selectivity of the reaction.[42] To increase the yield and selectivity of the epoxidation of olefins, the UHP was used as an oxidant, which had a good oxidation effect without producing diol, and the selectivity almost up to 100%.[43]

To evaluate the catalytic effect of rhenium ionic liquid [Smim][ReO_4] on epoxidation of olefin, the synthesized ionic liquid [Smim][ReO_4] was selected as a green solvent and catalyst, cyclohexene and cyclooctene were used as reaction substrates, and the UHP was selected as an oxidant in this paper for homogeneous catalyzed epoxidation of olefin. The reaction products were detected by gas chromatography (GC).

3. Results and Discussion

3.1 *Volume and surface properties of [Smim][ReO4]*

The values of density and surface tension within their experimental expanded uncertainty ± 0.0006 $g \cdot cm^{-3}$ and ± 0.3 $mJ \cdot m^{-2}$ at 0.95 confidence level for IL [Smim][ReO_4] are listed in Table 1, respectively.

The molecular volume, V_m, of [Smim][ReO_4] at 298.15 K, was calculated from the following equation:

$$V_m = M/(N \cdot \rho) \tag{1}$$

where the molar mass M of [Smim][ReO_4] is 431.552 $g \cdot mol^{-1}$ and N is Avogadro constant. The calculated value of V_m is listed in Table 2.

The standard entropy, S^0, and lattice energy, U_{POT}, of [Smim][ReO_4] were calculated by Glasser empirical equation, respectively:

$$S^0(298)/(J \cdot K^{-1} \cdot mol^{-1}) = 1246.5(V_m/nm^3) + 29.5 \tag{2}$$

$$U_{POT}/kJ \cdot mol^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \tag{3}$$

The calculated value of $S^0(298)$ and U_{POT} are also listed in Table 2. From Table 2, it is seen that the U_{POT} of [Smim][ReO_4] is much less than that of fused salt for fused CsI,[41] U_{POT} = 613 $kJ \cdot mol^{-1}$, which is the lowest crystal energy among alkali-chlorides. The low crystal energy is the underlying reason for forming ionic liquid at room temperature.

The contribution of per methylene (-CH_2-) to the molecular volume, standard entropy and lattice energy were obtained by plotting V_m, $S^0(298)$ and U_{POT} against the number (n) of carbons in alkyl chain with the [Smim][ReO_4] and reference data, respectively. The contribution values are also listed in Table 2, which are in accordance with the reference values, respectively.

The measured values of γ were fitted against T by the least square to linear empirical equation:

$$\gamma = A_0 - S_a \cdot T \tag{4}$$

where A_0 is an empirical parameter, the negative of slope in Figure 1 is the entropy of surface formation, $S_a = -(\partial\gamma/\partial T)_p = 50.0 \times 10^{-3}$ $mJ \cdot K^{-1} \cdot m^{-2}$ for [Smim][ReO_4] at 298.15 K.

Table 1. Values of density, ρ, and surface tension, γ, of IL [Smim][ReO_4] in the temperature range of 293.15-343.15 K[a], pressure p = 0.1 MPa[b].

T (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
ρ ($g.cm^{-3}$)	1.7340	1.7297	1.7243	1.7200	1.7145	1.7100	1.7062	1.7021	1.6980	1.6937	1.6900
γ ($mJ \cdot m^{-2}$)	37.8	37.6	37.4	37.1	36.9	36.7	36.4	36.1	35.9	35.6	35.3

Standard uncertainties (0.68 level of confidence): [a]$u(T)$ = ± 0.01 K for density and surface tension, [b]$u(p)$ = ± 0.002 MPa.

Table 2. The values of volume properties and surface properties of [Smim][ReO_4] and the contribution of per methylene (-CH_2-) at 298.15 K.

	V_m (nm^3)	S^0 ($J \cdot K^{-1} \cdot mol^{-1}$)	U_{POT} ($kJ \cdot mol^{-1}$)
[Smim][ReO_4]	0.4144	546.0	419
[a]-CH_2-	0.0275	34.2	9
-CH_2-	0.0275[b]	33.9[b]	10[c]

[a]Calculated by the experimental value of [Smim][ReO_4]; [b]reference 40 and 44; [c]reference 45.

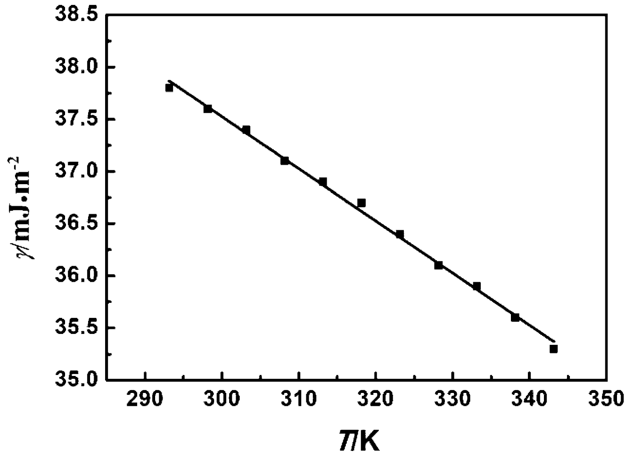


Figure 1. Plot of γ *vs*. T of [Smim][ReO$_4$].

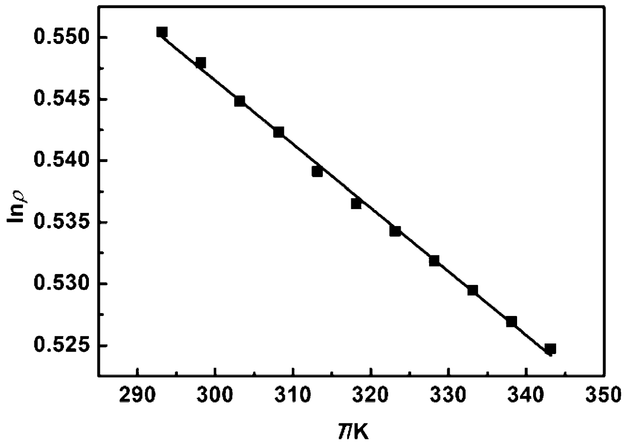


Figure 2. Plot of lnρ vs. T of [Smim][ReO$_4$].

Additionally, the Gibbs energy of surface formation E_a likewise may be obtained from the surface tension measured in this work:

$$E_a = \gamma - T(\partial\gamma/\partial T)_p \tag{5}$$

The calculated values of E_a are 52.5 mJ·m^{-2} for [Smim][ReO$_4$] at 298.15 K.

In comparison with fused salt for fused NaNO$_3$, E_a (298.15 K) = 146 mJ·m^{-2}, the value of E_a for [Smim][ReO$_4$] is much lower and is close to that of organic liquid, such as 67 mJ·m^{-2} (for benzene) and 51.1 mJ·m^{-2} (for n-octane).[46] This fact shows that interaction energy between ions in [Smim][ReO$_4$] is less than that in fused salts.

3.2 *The interstice model for [Smim][ReO$_4$]*

According to the definition of thermal expansion coefficient, α, of the IL:

$$\alpha = (1/V)(\partial V/\partial T)_p = -(\partial \ln\rho/\partial T)_p \tag{6}$$

Here, plotting of values of ln ρ against T (see Figure 2), and its empirical linear equation is:

$$\ln\rho = b - \alpha\cdot T \tag{7}$$

where b is an empirical constant, the negative value of slope is thermal expansion coefficient, $\alpha = -(\partial\ln\rho/\partial T)_p = 5.17\times10^{-4}$, and the experimental value of $\alpha_{(exp.)}$ is listed in Table 3.

Based on the classical statistical mechanics, the interstice model for pure ILs was put forward.[47] The interstice volume is expressed by the following equation:

$$v = 0.6791(k_b\cdot T/\gamma)^{3/2} \tag{8}$$

where v and k_b are the average interstice volume and Boltzmann constant, respectively. The average value of interstice volume was calculated by the above equation and listed in Table 3. All the interstices in the interstice model include the volume of IL, V, consists of the inherent volume, V_i, and total volume, $\sum v = 2N\cdot v$.

$$V = V_i + 2N\cdot v \tag{9}$$

Most of the materials undergo a (10-15.9) % volume expansion in the process from the solid to the liquid state.[48,49] The volume fraction of interstice for [Smim][ReO$_4$], $\sum v/V = 11.86\%$, is within the range of volume expansion, that is to say, the interstice model is suitable for the calculation of interstice volume for pure ILs. If the expansion of IL volume only results from the expansion of the interstices when temperature changes, then calculation expression of thermal expansion coefficients, α, was derived from the interstice model:

$$\alpha = (1/V)\cdot(\partial V/\partial T)_p = 3N\cdot v/V\cdot T \tag{10}$$

The value of $\alpha_{(cal.)}$ was calculated by Eq. (10) for IL [Smim][ReO$_4$] at 298.15 K. From Table 3, the magnitude order of the calculated value is in good agreement with its matching experimental value, $\alpha_{(exp.)}$. It means that the interstice model for pure ILs is reasonable and rational.

3.3 *Catalytic properties for the IL*

Epoxidation of olefins stands out as a crucial class of reactions and is of great interest in academic research

Table 3. Parameters of interstice model for IL [Smim][ReO_4], at 298.15 K.

10^{24} v (cm^3)	$\sum v$ (cm^3)	V ($cm^3 \cdot mol^{-1}$)	$10^2 \sum v/V$	10^4 α/K^{-1} (cal.)	10^4 α/K^{-1} (exp.)
24.58	29.59	249.5	11.86	5.97	5.17

and industry due to the production of various important fine chemicals and intermediates. Rhenium containing compounds have the potential to catalyze the epoxidation of olefins with high efficiency. In this section, the IL [Smim][ReO_4] was used as catalyst and solvent. At a given temperature, a certain amount of IL was added to the catalytic evaluation unit, then oxidant UHP was added and stirred slowly until all UHP dissolved, and the cyclohexene or cyclooctene as the substrate, respectively, after that the homogeneously catalyzed epoxidation of olefin was established. The mixture was quickly stirred under cooling for a certain period until the oxidation reaction finished, which was extracted with n-hexane for 3 times at 50 °C. Finally, the upper clear liquid was detected by gas chromatography and the results were calculated by normalization method. Figure 3 is the reaction equation of olefin epoxidation in IL [Smim][ReO_4].

Orthogonal experimental was designed by the influence of catalyst of [Smim][ReO_4], oxidant of UHP, reaction time and temperature on the yields, which is shown in Figure 4.

Figure 4 is shown that the influence degree of the four factors for the yields as follows: the substrate was used as the cyclohexene or cyclooctene, these factors decreased in the order of reaction temperature > reaction time > oxidant (UHP) dosage > catalyst ([Smim][ReO_4]) dosage or reaction time > reaction temperature > oxidant (UHP) dosage > catalyst ([Smim][ReO_4]) dosage, respectively.

According to the above orthogonal experimental results, further detailed conditional optimization experiments were done (Table 4). And, the results are similar to those of the orthogonal experiment.

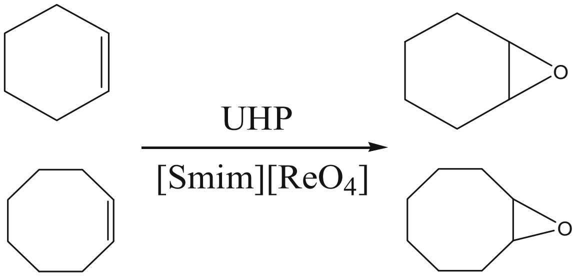


Figure 3. Olefin epoxidation in IL [Smim][ReO_4].

In general, the yields of olefin epoxidation will gradually increase with increasing the reaction temperature and time, and the amount of IL and UHP, respectively, but it does not mean the higher the better. For instance, the higher reaction temperature will affect the thermal stability of UHP. The yields little increase with increasing time, when reached more than 96% or 98%. Besides, the solubility of UHP in IL is limited and the homogeneous catalytic system will be destroyed by excessing it. When the content of [Smim][ReO_4] is 0.4 mL, the concentration of catalyst and active center in the reaction system was low, which led to poor catalytic efficiency. Additionally, the IL [Smim][ReO_4] is not only the catalyst but also solvent in this reaction system. The substance was not dissolved sufficiently in the relatively less solvent that results in a slow reaction rate and relatively low yield. At the same time, increasing the content of IL will increase and improve the catalytic efficiency, but excess IL will reduce the concentration of reactants, which is of no advantage to the reaction. Herein, the concentration of the catalyst reached saturation state as the amount of [Smim][ReO_4] is more than 0.6 mL, at which point the yield is independent of the catalyst concentration. Moreover, the reactant was diluted by the excess solvent and the concentration was reduced, resulting in the reaction rate and yields were relative reduced.

Based on previous work of our team and DFT calculations,[50] the transfer of perrhenate from the aqueous to hydrophobic organic phase should activate H_2O_2 through H-bonding interactions, which in turn favours oxygen transfer to an olefin. Because the structure of the hydroxyl bond in UHP is similar to that of H_2O_2, we predict the mechanism of the epoxidation of olefins catalysed by [Smim][ReO_4]. For example, the mechanism diagram (Scheme 2) describes the epoxidation of cyclohexene. In this reaction, UHP is presumably associated with the IL anion. Hydrogen bonds to the cation probably do not form in the presence of a potent H-bond acceptor (perrhenate anion). The addition of metal—oxo complexes, such as $[ReO_4]^-$, accelerates the reaction, presumably through the formation of $O_3Re—O\cdots H–O—OH$ species, which activate the peroxide and, hence, enable epoxidation.

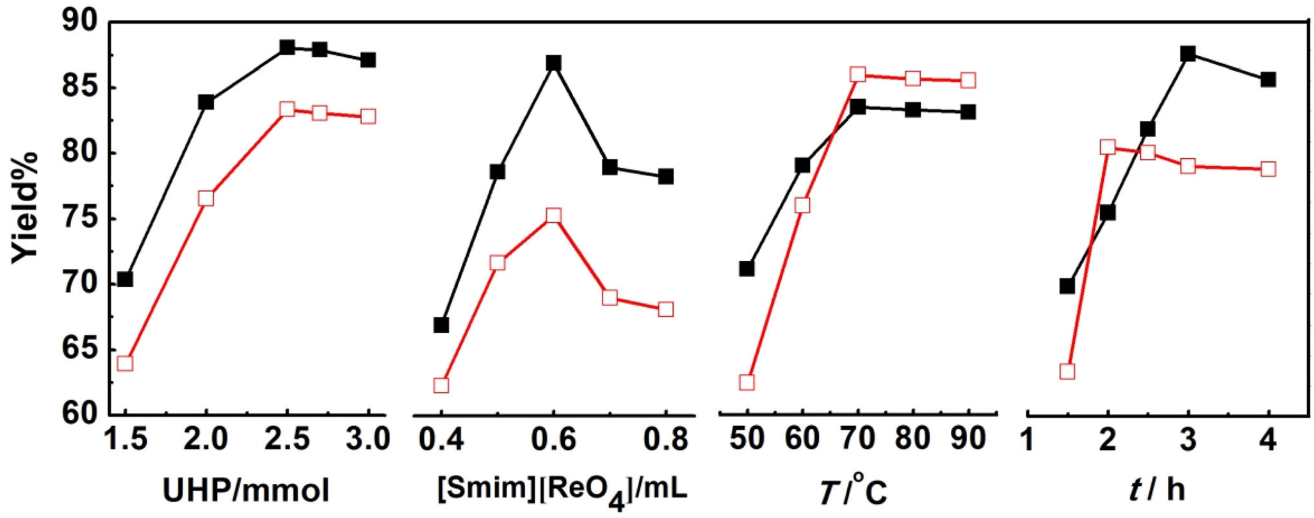


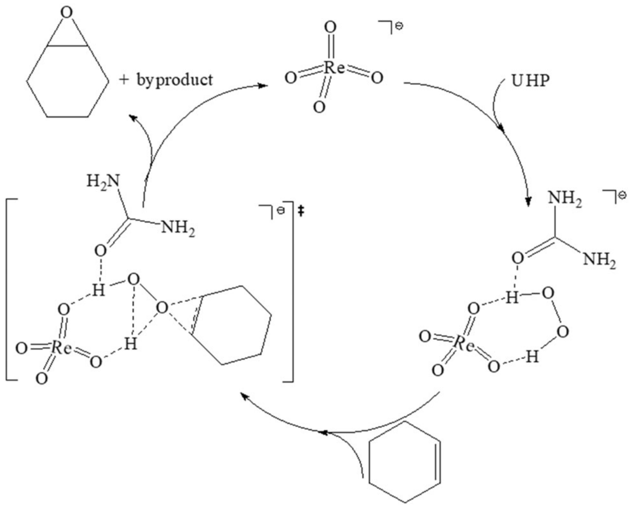
Figure 4. Four factors affect the yields for substrates of cyclohexene (black solid symbols) and cyclooctene (red hollow symbols).

Table 4. Conditional optimization experiments of olefin epoxidation in IL [Smim][ReO_4].

No.	Substrate	UHP/mmol	[Smim][ReO_4] (mL)	*T* (°C)	*t* (h)	*Y* (%)	*S* (%)
1	cyclohexene	2	0.6	70	3	98.35	> 99
2		2.5	0.6	70	3	> 99	> 99
3		3	0.6	70	3	> 99	> 99
4		2.5	0.6	70	2.5	96.87	> 99
5		2.5	0.6	70	3	> 99	> 99
6		2.5	0.6	70	3.5	> 99	> 99
7		2.5	0.6	65	3	97.64	> 99
8		2.5	0.6	70	3	> 99	> 99
9		2.5	0.6	75	3	98.52	> 99
10		2.5	0.55	70	3	97.45	> 99
11		2.5	0.6	70	3	> 99	> 99
12		2.5	0.65	70	3	98.18	> 99
13	cyclooctene	2	0.6	70	2	97.56	> 99
14		2.5	0.6	70	2	> 99	> 99
15		3	0.6	70	2	> 99	> 99
16		2.5	0.6	70	1.5	95.93	> 99
17		2.5	0.6	70	2	> 99	> 99
18		2.5	0.6	70	2.5	> 99	> 99
19		2.5	0.6	65	2	98.08	> 99
20		2.5	0.6	70	2	> 99	> 99
21		2.5	0.6	75	2	97.89	> 99
22		2.5	0.55	70	2	96.28	> 99
23		2.5	0.6	70	2	> 99	> 99
24		2.5	0.65	70	2	98.37	> 99

T: temperature, °C; *t*: reaction time, h; *Y*: yield; *S*: selectivity of target epoxide = (moles of target epoxide formed)/(moles of all the products formed) × 100%.

The optimum reaction conditions were decided by orthogonal experimental, as follows: oxidant (UHP) dosage is 2.5 mmol, catalyst/solvent ([Smim][ReO_4]) dosage is 0.6 mL, reaction temperature is 70 °C, and reaction time is 3 h or 2 h for cyclohexene or cyclooctene, respectively. To prove the universality of the catalyst, we studied on the epoxidation of other alkenes. These results are listed in Table 5, which



Scheme 2. Mechanism of the epoxidation of olefins catalysed by [Smim][ReO_4].

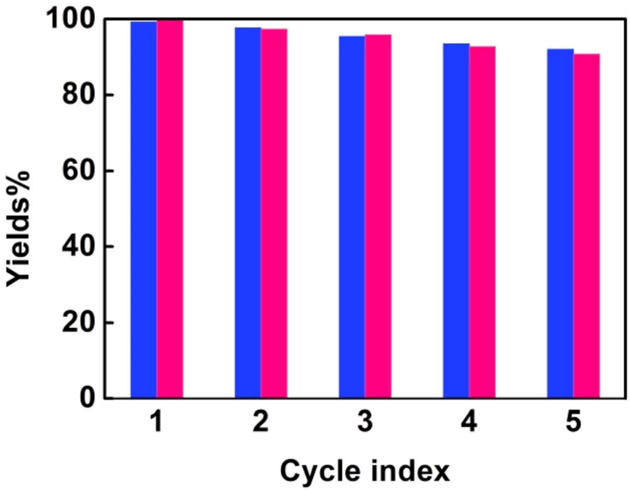


Figure 5. The recycling efficiency of IL [Smim][ReO_4] affects the yields with the substrates of cyclohexene (blue) and cyclooctene (pink).

shown that the reaction with the high conversion rate. The reason for the relatively low conversion of other alkenes may be that the terminal and open-chain olefins are more difficult to epoxidize than cyclic olefins.[38] Based on the optimum reaction conditions, the conversion and selectivity of cyclohexene and cyclooctene are over 99%.

Furthermore, the reusability of IL [Smim][ReO_4] was investigated. A certain amount of ultrapure water was added in the lower liquid containing the [Smim][ReO_4], then the mixed solution was quickly stirred for some time at room temperature and separated after static. Repeat this operation 5 times, the mixture containing [Smim][ReO_4] and a small amount of water was evaporated under reduced pressure at 80 °C. Subsequently, the [Smim][ReO_4] could be reused after drying under vacuum for 3 h.

From Figure 5, it is shown that the catalytic efficiency of [Smim][ReO_4] did not decrease significantly after five times recycling, and the yields still reach 90%, while the selectivity of epoxides is up to 99%. The yields decreased with increasing recycle times of [Smim][ReO_4], which is due to the loss of catalyst during recovery.

Table 5. The optimum reaction conditions were selected by orthogonal experimental.

No	Substrate	Catalyst	Oxidant	*T* (°C)	*t* (h)	*Y* (%)	*S* (%)	Ref.
1	cyclohexene	–	UHP	70	3	9.2	3.1	This work
2	cyclooctene	–	UHP	70	2	10.3	2.8	This work
3	cyclohexene	[Smim][ReO_4]	UHP	70	3	> 99	> 99	This work
4	cyclooctene	[Smim][ReO_4]	UHP	70	2	> 99	> 99	This work
5	cyclooctene	$KReO_4$	H_2O_2	70	6	97	–	[35]
6	cyclooctene	[Me_3NHex][ReO_4]	H_2O_2	70	24	91	> 99	[38]
7	cyclooctene	[OMIM]$_2$[WO_4]	H_2O_2	50	8	81	99	[51]
8	cyclohexene	Mo-VPO	TBHP	90	10	100	91	[27]
9	cyclohexene	LDH/Ti(IV)-complex	H_2O_2	70	6	95	84	[20]
10	cyclohexene	SIP [HL^1][ReO_4]	H_2O_2	70	8	89	99	[36]
11	Styrene	[Smim][ReO_4]	UHP	70	6	73	54	This work
12	Allyl alcohol	[Smim][ReO_4]	UHP	70	6	88	23	This work
13	1-Octene	[Smim][ReO_4]	UHP	70	6	83	39	This work
14	1-Dodecene	[Smim][ReO_4]	UHP	70	6	72	48	This work

The amount of substrate for cyclohexene and cyclooctene was 1 mmol, respectively; UHP: 2.5 mmol, [Smim][ReO_4]: 0.6 mL *T*: temperature, °C; *t*: reaction time, h; *Y*: yield; *S*: selectivity of target epoxide = (moles of target epoxide formed)/(moles of all the products formed) × 100%.

4. Conclusions

In this paper, we have synthesized and characterized summarized the novel IL based on catalytic functional metal rhenium, [Smim][ReO_4] (1-heptyl-3-methylimidazolium perrhenate). The physicochemical properties, such as density, ρ, surface tension, γ, molecular volume, V_m, standard entropy, S^0, lattice energy, U_{POT}, the entropy of surface formation, S_a, and the Gibbs energy of surface formation, E_a, were obtained and discussed, respectively. Furthermore, the synthesized ionic liquid [Smim][ReO_4] was used as a green solvent and catalyst for homogeneous catalyzed epoxidation of olefin with UHP oxidant. The results showed that the yield and selectivity of the reaction were up to 99%, and the catalytic efficiency of [Smim][ReO_4] did not decrease significantly after five times recycling. Easy separation, recycle, nontoxicity and homogeneous catalysis are the main advantages of perrhenate ionic liquids over other heterogeneous catalysts containing organic solvents. Consequently, the perrhenate ionic liquids will have wide industrial application prospect.

Supplementary Information (SI)

Figures S1-S3 are available at www.ias.ac.in/chemsci.

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