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Green Oxidation of Cyclohexene to Adipic Acid with Hydrogen Peroxide Catalyzed by 12-Phosphotungstate acid and Ionic Liquids

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Heteropoly acids (HPAs) are very attractive since their acidic and redox properties can be controlled at atomic or molecular levels.^[1] Among various HPAs structural classes, the Keggin-type HPAs containing tungstate and molybdenum have been widely employed not only for oxidation of organic substrates but also for many acid-catalyzed reactions due to their strong oxidizing ability and acid strength^[2]. Selective oxidation of lower hydrocarbons is of fundamental and technological interest because it provides a potential route to effectively transform lower hydrocarbon to higher, value-added chemicals^[3,4]. There have been a number of procedures for oxidation cleavage of hydrocarbons using H₂O₂ and in situ generated or preformed molybdenum and tungsten complexes^[5-7] since H₂O₂ is cheap and environmentally benign. These molybdenum and tungsten complexes including phase-transfer catalyst, usually the quaternary ammonium such as [C₆H₅CH₂N(C₂H₅)₃]Cl and π -C₅H₅NC₁₆H₃₃Br, have been proved to be the most efficient catalysts for oxidation cleavage reactions. Ionic liquids (ILs), composed of organic nitrogen-containing heterocyclic cations and inorganic or organic anions, are also viewed as quaternary ammoni-

um. Compared with [C₆H₅CH₂N(C₂H₅)₃]Cl and π -C₅H₅NC₁₆H₃₃Br, ionic liquids are designable and more environmentally benign. Ionic liquids have attracted considerable attention in the past due to their unique chemical and physical properties, such as high chemical and thermal stability, negligible vapor pressure, high conductivity, and the ability to dissolve a wide range of organic and inorganic compounds^[8]. So far, ionic liquids have been used in various research fields including organic synthesis^[9], catalysis^[10], and extraction^[11]. Here, we report the oxidation of cyclohexene to adipic acid (AA) catalyzed by 12-phosphotungstate acid and ionic liquids in situ with 30% hydrogen peroxide.

1 Experimental

All chemicals and reagents used in the present study were of analytical grade. Organic solvents were freshly distilled and purified before used. IR spectra were recorded on a FT-IR Bruker IFS 120HR spectrophotometer with KBr pellets. NMR spectral characterization was carried out with an INOVA-400 MHz instrument operating near 400(¹H) and 100(¹³C) MHz.

12-Phosphotungstate acid (HPW) was prepared

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according to the methods reported in the literatures^[12]. Ionic liquids (shown in Table 1) were synthesized according to the procedures reported in the literatures^[13-15]. All of them were confirmed by infrared spectroscopy and ionic liquids were further confirmed by ¹³C NMR, ¹H NMR.

The catalytic reaction was performed in a dry 250 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. Then HPW, ionic liquids and hydrogen peroxide was encased into the flask under stirring in a ranged order at room temperature. Cyclohexene was added to the mixture after ca. 15 min. The whole mixture was allowed to react at reflux temperature of 70 ~ 90 °C for 8 h and then the homogeneous solution was allowed to stand at 4 °C for 24 h. A white precipitate was separated by filtration and washed with 20 mL ice water. After drying at room temperature the product AA was gained with mp 152 ~ 153 °C, and calculated by isolated yield.

Table 1 the influence of ionic liquids with different amount on the reaction^a

IL ^b	Isolated yield (%)			
	IL/HPW (mol ratio) ^b			
	1/2	1/1	2/1	3/1
[(CH ₂) ₄ SO ₃ H-mim][HSO ₄]	70.2	70.5	72.8	68.0
[(CH ₂) ₄ SO ₃ H-Py][HSO ₄]	70.5	73.8	84.9	71.8
[Hmim][p-CH ₃ (C ₆ H ₄)SO ₃]	73.2	76.0	74.5	65.1

^a Reaction conditions: $n_{(\text{cyclohexene})} : n_{(\text{H}_2\text{O}_2)} : n_{(\text{HPW})} = 1 : 4.4 : 0.28$, cyclohexene

100 mmol, reflux temperature, reaction time 8 h; ^bIonic liquid was added in manner (I)

kept clear throughout the reaction for all ionic liquids and ionic liquids used in this manner must play different role compared with (I) in the reaction. They may

2 Results and Discussion

Initially, we discovered that the ionic liquid's addition manner greatly influence the reaction. There were two kinds of addition manner used in this study. In manner (I), HPW and ionic liquids were mixed first and then hydrogen peroxide was added. The solution obtained in this manner becomes cloudy which indicating some transformation has occurred. For usual 1, 3-dialkylimidazolium salts, no changes took place when hydrogen peroxide was added in and no product AA was obtained indicating the compounds formed in situ could not catalyze the reaction^[16]. But for SO₃H-functionalized ionic liquids and 1-methylimidazolium (abbreviate as Hmim below) salts, the compounds formed in situ can dissolve into the solution and the results were good (see Table 1). In manner (II), ionic liquids were added after HPW have reacted with hydrogen peroxide. The solution obtained in this manner

act as phase transfer catalyst and can adjust the acidity of the system.

As shown in Table 2, the ionic liquids chosen

Table 2 The results of cyclohexene oxidation catalyzed by HPW-IL system^a

No.	IL ^b	IL/HPW (mol ratio)	Isolated yield (%)
1	-	-	55.0
2	[C ₄ mim]Br	3/1	56.7
3	[C ₈ mim]Br	3/1	72.3
4	[C ₁₆ mim]Br	3/1	36.3
5	[C ₄ mim]BF ₄	3/1	66.0
6	[C ₈ mim]BF ₄	3/1	70.7
7	[Hmim][HSO ₄]	3/1	57.7
8	[Hmim][H ₂ PO ₄]	3/1	55.2
9	[Hmim][p-CH ₃ (C ₆ H ₄)SO ₃]	3/1	66.9
10	[(CH ₂) ₄ SO ₃ H-mim][HSO ₄]	3/1	69.4
11	[(CH ₂) ₄ SO ₃ H-Py][HSO ₄]	3/1	74.1

^a Reaction conditions: $n_{(\text{cyclohexene})} : n_{(\text{H}_2\text{O}_2)} : n_{(\text{HPW})} = 1 : 4.4 : 0.28$, cyclohexene 100 mmol,

reflux temperature, reaction time 8 h; ^b Ionic liquid was added in manner(II)

have shown different influences on the oxidation reaction of cyclohexene in manner (II). For 1,3-dialkylimidazole bromide salts, $[\text{C}_8\text{mim}]\text{Br}$ gave 72.3% isolated yield of AA (entry 3) while $[\text{C}_{16}\text{mim}]\text{Br}$ gave 36.3% (entry 4) showing that the increase of carbon number of the alkyl substitution do not always brought good result. When the anion changed, $[\text{C}_4\text{mim}]\text{BF}_4$ showed some extent of improvement compared with $[\text{C}_4\text{mim}]\text{Br}$, but $[\text{C}_8\text{mim}]\text{BF}_4$ kept the same level with $[\text{C}_8\text{mim}]\text{Br}$. The Brønsted acidic ionic liquid $[\text{Hmim}]\text{X}$ ($\text{X} = \text{HSO}_4, \text{H}_2\text{PO}_4, \text{p-CH}_3(\text{C}_6\text{H}_4)\text{SO}_3$) were examined too. Among these three ionic liquids, $[\text{Hmim}][\text{p-CH}_3(\text{C}_6\text{H}_4)\text{SO}_3]$ performed better result probably due to its stronger lipophilic property^[17]. The SO_3H -functionalized ionic liquids with pyridine cation (entry 11) gave 74.1% isolated yield of AA while $[(\text{CH}_2)_4\text{SO}_3\text{H-mim}][\text{HSO}_4]$ gave 69.4% (entry 10) under the same condition.

The influence of SO_3H -functionalized and 1-methylimidazolium ionic liquids with different amount on the oxidation reaction is shown in Table 1. From Table 1 we can see that as the IL/HPW mol ratio increased but under 2/1, the reaction showed better results. $[(\text{CH}_2)_4\text{SO}_3\text{H-Py}][\text{HSO}_4]$ gave the best isolated yield of 84.9% with a mol ratio 2/1 with HPW. This results can compared with the previous literature^[18,19,20]. Ionic liquid $[(\text{CH}_2)_4\text{SO}_3\text{H-mim}][\text{HSO}_4]$ in the same condition gave an isolated yield of 72.8%, which is basically the same level of mol ratio at 0.5/1 and 1/1. $[\text{Hmim}][\text{p-CH}_3(\text{C}_6\text{H}_4)\text{SO}_3]$ gave the isolated yield of 76.0% at mol ratio 1/1, which is better than mol ratio at 1/2 and 2/1. Keeping on increasing the amount of ionic liquids (mol ratio with HPW achieve 3/1) no more improvement could be seen, which also indicated that two kinds of addition manner showed little influence on the oxidation reaction with SO_3H -functionalized and 1-methylimidazolium ionic liquids compared with Table 2.

We also investigated the reusability of the catalysts system. As one of the most effective catalyst system, HPW- $[(\text{CH}_2)_4\text{SO}_3\text{H-Py}][\text{HSO}_4]$ was chosen to check its reusability. After each reaction, the homogeneous solution was allowed to stand at 4°C for 24 h,

and the resulting white precipitate was separated by filtration and washed with 20 ml of cold water. The mother liquor was concentrated and then allowed to stand at 4°C for 24 h, and the resulting white precipitate was separated as the same. The mother liquor was concentrated again to 5 ml and then encased in to the reaction flask with fresh hydrogen peroxide for the next use. This procedure was repeated for 4 cycles. The results were shown in figure 1. It can be seen that the catalytic activity was slightly decreased, and it was stable to ensure 4 uses.

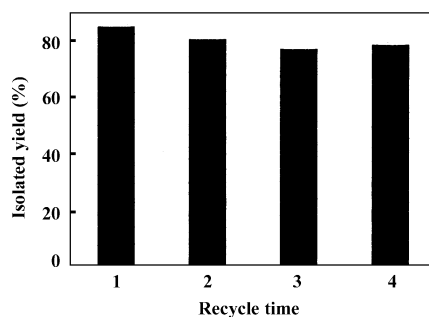


Fig. 1 HPW- $[(\text{CH}_2)_4\text{SO}_3\text{H-Py}][\text{HSO}_4]$ system for recycle

3 Conclusion

In summary, the use of ionic liquids have different effect on the catalytic reaction of cyclohexene. Among various ILs, the SO_3H functional IL $[(\text{CH}_2)_4\text{SO}_3\text{H-Py}][\text{HSO}_4]$ in the mol ratio of 1/2 with HPW gave adipic acid of isolated yield with 84.9% and this catalyst system can use 4 times with a slightly decrease of activity.

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杂多酸和离子液体催化环己烯的清洁氧化反应研究

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摘 要:以 30% 过氧化氢为氧化剂, 考察了以杂多酸为催化剂氧化环己烯过程中离子液体的作用, 讨论了离子液体种类和用量对反应的影响. 结果表明, 离子液体的加入顺序不同, 其在催化过程中所起的作用不同. 在反应条件为 $n(\text{环己烯}) : n(\text{过氧化氢}) : n(\text{磷钨酸}) : n([\text{(CH}_2\text{)}_4\text{SO}_3\text{H-Py}][\text{HSO}_4]) = 1 : 4.4 : 0.28 : 0.56$, 在回流温度下反应 8 h 时, 己二酸收率可达到 84.9%. 该催化剂体系可循环使用.

关键词:杂多酸; 离子液体; 氧化; 环己烯