



The oxidation of pyridine and alcohol using the Keggin-type lacunary polytungstophosphate as a temperature-controlled phase transfer catalyst

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ABSTRACT

A novel temperature-controlled phase transfer catalyst of $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ has been developed for the oxidation of pyridines and alcohols with hydrogen peroxide. The reactions were conducted in 1,4-dioxane, and high yields of the corresponding heterocyclic N-oxides and ketones were obtained under relative mild conditions. The catalyst could be easily recovered and reused after reaction with cooling. There was no discernable loss in activity and selectivity after several reaction cycles.

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1. Introduction

The oxidation of pyridines to the corresponding N-oxides is an important chemical procedure due to the wide usefulness of the products. Heterocyclic N-oxides have important roles in organic synthesis, which are used as protecting groups, auxiliary agents, oxidants, catalysts, surrogates for heterocyclic boronic acids and ligands in metal complexes [1–4]. These oxides usually are prepared by a non-catalytic oxidation process using peracids [5], H_2SO_5 [6], dioxiranes [7] and magnesium monophthalate [8]. From the green chemistry and the need for chemical industry to minimize waste production associated with stoichiometric reagents, catalytic oxidation systems using hydrogen peroxide as oxidant with active catalysts have been developed recently, such as $AcOH/H_2O_2$ [9], $MeReO_3/H_2O_2$ [10], trifluoroacetic anhydride (TFAA)/ H_2O_2 [11] and $Tf_2O/Na_2CO_3 \cdot 1.5H_2O_2$ [12]. However, the catalysts in these active systems are not reusable. Some heterogeneous catalysts like perfluoroketone-silicate [13], TS-1 [14] and $V_xSi_{4x}O_{6,4x}$ [15] were also demonstrated for the oxidation of pyridines. But in these heterogeneous systems, the high reaction temperature or the long reaction time is required. So the design of a new recyclable, effective and green catalytic system for pyridine oxidation is still necessary.

Carbonyl compounds are important group of molecules in organic chemistry [16–18]. The selective oxidation of alcohols to

the corresponding carbonyl compounds is a key transformation in organic synthesis. Most examples of alcohol oxidation with hydrogen peroxide employed polyoxometalates as catalysts have been reported [19–26]. Recently, the catalytic oxidation of alcohols using recyclable catalysts has received much attention, such as reaction-controlled phase transfer catalysts [27,28], water-soluble polyoxometalates [29–35], polymer-supported catalysts [36,37] and inorganic-organic hybrid mesoporous materials [38]. These catalytic systems were active for alcohol oxidation, and the catalysts were all reusable after reaction. However, these procedures have some of the following disadvantages: the recovery of the catalysts was controlled by the amount of H_2O_2 , the reused catalysts were difficult to obtain, some solid alcohols or hydrophobic alcohols were hardly reactive or the catalyst was not easy to synthesize. The search for new, facile, cost-effective, and environmentally benign procedures that avoid the use of toxic solvent and expensive oxidant still attracts substantial interest.

We tried to design a reusable catalytic system for pyridine oxidation and alcohol oxidation based upon temperature-dependency. Some methods have been explored for the recovery and reuse of the catalyst by controlling temperature, such as the temperature-dependent multi-component solvent systems [39] and the protocols based on temperature-dependent solubilities of fluorine compounds [40]. Herein, we firstly report a recyclable and effective catalytic system for pyridine N-oxidation and alcohol oxidation based on a temperature-controlled phase transfer catalyst. The catalyst was synthesized by lacunary Keggin phosphotungstate anion combined with dioctadecyl dimethyl ammonium

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Table 1
Oxidation of 2-picoline under different solvents catalyzed by $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ with hydrogen peroxide.^a

Entry	Solvent	Solubility of catalyst		Yield ^b (%)
		During reaction (65 °C)	After reaction (25 °C)	
1 ^c	1,4-Dioxane	–	–	9
2	1,4-Dioxane	Soluble	Insoluble	98
3	Ethanol	Soluble	Insoluble	59
4	Acetonitrile	Soluble	Insoluble	85
5	Acetone	Soluble	Insoluble	80
6	Ethyl acetate	Soluble	Insoluble	93
7	Toluene	Soluble	Soluble	94
8	1,2-Dichloroethane	Soluble	Soluble	98

^a Reaction conditions: 1 mmol substrate, 5 mmol (30% aq.) H_2O_2 , 8 μ mol catalyst, 2 ml solvent, 65 °C, 3 h.

^b Yields were determined by GC analysis. Selectivity to the N-oxide was $\geq 99\%$. Assignments of products were analyzed by 1H NMR and ^{13}C NMR.

^c Without catalyst.

ion, $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$, and it has temperature-responsive behavior in a biphasic mixture of aqueous H_2O_2 and 1,4-dioxane. The catalyst was insoluble in the system at room temperature, but dissolved with the elevation of reaction temperature. After the reaction finished with cooling, the catalyst precipitated gradually from the system itself. The catalyst effectively catalyzed the oxidation and could be easily recovered and reused.

2. Experimental

2.1. Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

2.2. Preparation of the catalyst $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$

First 30 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 37 ml of distilled water with stirring. Then 0.75 ml of 85% H_3PO_4 , followed by 5.5 ml of glacial acetic acid, was added to the stirring solution. After a few seconds the solution became cloudy and after about 1 min a heavy white precipitate had formed. The solid was collected and first dried under aspiration for 24 h, and then the aspirated solid was left in air for 24 h [41]. After that, the solid was dried at 140 °C for about 1.5 h. Then, 0.56 g of the dried solid was dissolved in 55 ml of water. To this solution, 0.9 g of dioctadecyl dimethyl ammonium chloride dissolved in 10 ml of tert-butanol was added slowly. The mixture was stirred vigorously for 4–5 h at 40 °C. A white solid was filtered off and then washed with an excess amount of water, then dried in vacuum. The yield was 85%. IR spectrum (KBr, cm^{-1}): 1079, 1040, 945, 900, 849, 806, 759, 725, 591, 512, 409. ^{31}P MAS NMR: –10.2 ppm. Calcd. for $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$: C, 48.90; H, 8.58; N, 1.50; P, 0.47; W, 30.98. Found: C, 50.03; H, 8.76; N, 1.47; P, 0.43; W, 30.89.

2.3. Characterization techniques

Infrared spectra were recorded on a Nicolet FTIR-360 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding. ^{31}P MAS NMR spectra were recorded at 9.4 T on a Bruker Avance-400 wide bore spectrometer. The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz with BB MAS probe head using 4 mm ZrO_2 rotors and 3.8 μs pulse and 2 s repetition time and 4096 scans, with samples spun at 10 kHz and referenced to 85% H_3PO_4 . GC analyses were performed on Shimadzu GC-9AM with a flame ionization detector equipped with SE-54 capillary (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (inter-

nal diameter = 0.25 mm, film thickness = 0.25 μm , length = 30 m). Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (IRIS ER/S), and C, H, and N contents were measured on a German Elementar Vario EL spectrometer.

2.4. Catalytic reaction

Catalyst (8 μ mol), 1,4-dioxane (2–3 ml), substrate (1 mmol), and H_2O_2 (5 mmol, 30% aq.) were charged in the reaction flask. The reaction was carried out at proper temperature for 3–7 h. After reaction finished with temperature dropping, the catalyst precipitated itself from the solvent. The catalyst was separated by centrifugation and washed with Et_2O , which was then used for the next oxidation. The organic products were separated from the aqueous phase by extraction and then the organic layer was analyzed by GC with the internal standard method. Assignments of some products were made by comparison with authentic samples. Selective products were obtained by evaporation or column chromatography and analyzed by IR, melting point, 1H NMR and ^{13}C NMR.


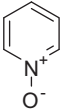

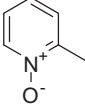
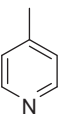
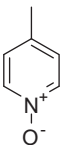
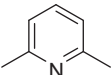
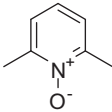
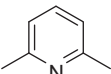
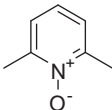
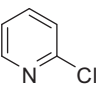
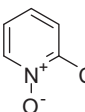
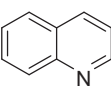
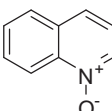
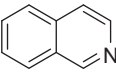
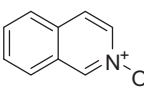
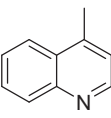
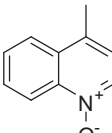
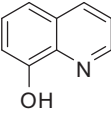
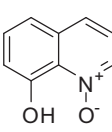
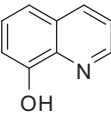
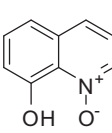
3. Results and discussion

3.1. Pyridine oxidation

Using the temperature-controlled phase transfer catalyst, we investigated the effect of the solvent on temperature phase transformation for the oxidation of 2-picoline with hydrogen peroxide (Table 1). Although the catalyst of $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ was insoluble in most solvents at room temperature, a homogeneous medium was formed in all solvents during the oxidation at reaction temperature (65 °C). After the reaction with cooling, the catalyst precipitated gradually from the system in some solvents, including 1,4-dioxane, ethanol, acetonitrile, acetone and ethyl acetate. In contrast, the catalyst was still soluble in toluene and 1,2-dichloroethane when the temperature cooled to the room temperature after reaction. The catalytic results for the oxidation of 2-picoline to 2-picoline-N-oxide under different solvents are also summarized in the table. The oxidation was effectively catalyzed in most solvents investigated in short reaction time, and the N-oxide was the only product. Especially in 1,4-dioxane and 1,2-dichloroethane, excellent yields of the N-oxide were obtained (Table 1, entries 2 and 8). Considering that the catalyst could not be reused in 1,2-dichloroethane, 1,4-dioxane was chosen as the optimal solvent in this catalytic system. In addition, a control experiment was also conducted in 1,4-dioxane with H_2O_2 in the absence of catalyst. Only 9% yield of the product was observed; indicating the strong activity of the catalyst used in this system.

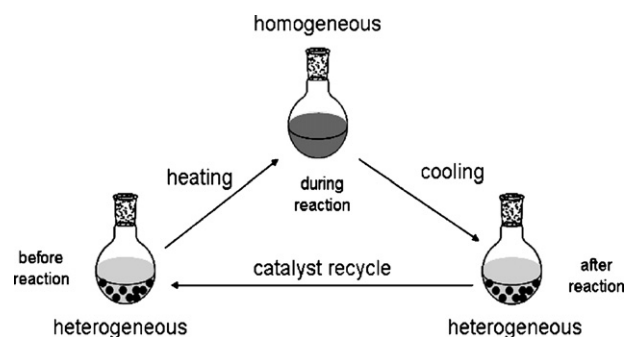
Having obtained these results, we extended our temperature-controlled phase transfer catalytic system to the oxidation of other pyridine derivatives. The results are listed in Table 2. The yields

Table 2
Oxidation of pyridine derivatives with H₂O₂ catalyzed by [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉].^a

Entry	Substrate	Product	Time (h)	Yield (%)
1			3	99
2			3	98
3			3	94
4			3	62
5			6	84
6			6	55
7			3	95
8			3	87
9			3	83
10			3	80
11			6	95

^a Reaction conditions: 1 mmol substrate, 5 mmol (30% aq.) H₂O₂, 8 μmol catalyst, 2 ml 1,4-dioxane, 65 °C. Yields were determined by GC analysis. Selectivity to the N-oxide was ≥99%. Assignments of products were analyzed by ¹H NMR and ¹³C NMR.

were high to excellent for some representative substrates in short reaction time such as pyridine, 2-picoline, 4-picoline, quinoline, isoquinoline and 4-methyl-quinoline. Selectivities to the N-oxides were ≥99%. Electron-deficient substrate like 2-chloropyridine was hardly reactive as expected (Table 2, entry 6). Interestingly, 2,6-

**Fig. 1.** Representation of the temperature-controlled phase transfer catalytic system.

lutidine was less reactive than other substrates, this should be attributed to the steric considerations. Increasing the reaction time from 3 h to 6 h led to a good yield in N-oxidation product formation (Table 2, entries 4 and 5). 8-Hydroxyquinoline was also the same case with the steric effect of the –OH group, but an excellent yield (95%) of the desired product was obtained when the reaction time increased to 6 h.

The catalyst could be easily recycled in this system. Representation of the temperature-controlled phase transfer catalytic system is shown in Fig. 1. At the beginning of the reaction, the catalyst was insoluble in the solvent of 1,4-dioxane at room temperature. When the oxidation was carried out with heating, the catalyst dissolved in the system gradually. After the reaction finished with the temperature dropping, the system gradually changed from clear to turbid and the catalyst precipitated itself from the system. The catalyst could be separated from the system by centrifugation and used for the next cycle. Table 3 lists the catalytic activity in oxidation of 2-picoline based on [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉] for different cycles. As shown in the table, the catalytic activity and selectivity of the recovered catalyst were almost the same as those of the fresh catalyst. A 97% yield of 2-picoline-N-oxide could be achieved even after six cycles, indicating the excellent and stable activity of the catalyst is.

3.2. Alcohol oxidation

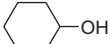
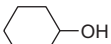
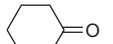
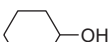
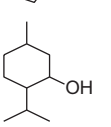
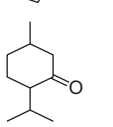
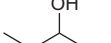
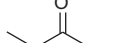

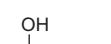

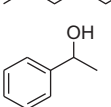
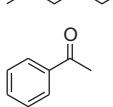
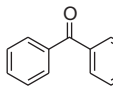
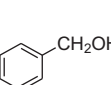
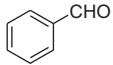
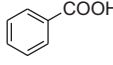
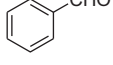
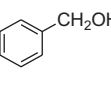
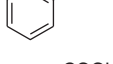
Table 4 summarizes the results of catalytic oxidation of various alcohols in water with 30% H₂O₂ based on [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉]. During the reaction with heating, the catalyst dissolved in the system and catalyzed the oxidation of alcohols. As shown in Table 4, several secondary alcohols were successfully oxidized to the corresponding ketones in high conversion and selectivity. Liquid cyclic alcohols, cyclohexanol and cyclopentanol were converted to the corresponding ketones with the 98% and 96% yields, respectively. For linear aliphatic alcohols, it was found that the shorter linear alcohol (2-pentanol) was more active than the longer one (2-octanol) in this oxidation system. A yield of 97% was also obtained in oxidation of the benzylic sec-

Table 3
Recycling of the catalytic system for the oxidation of 2-picoline.^a

Cycle	Time (h)	Conversion (%)	Yield (%)
1	3	99	98
2	3	99	98
3	3	98	97
4	3	99	98
5	3	99	98
6	3	98	97

^a Reaction conditions: 1 mmol substrate, 5 mmol (30% aq.) H₂O₂, 8 μmol catalyst, 2 ml 1,4-dioxane, 65 °C. Yield to the N-oxide.

Table 4
Oxidation of various alcohols catalyzed by $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ with H_2O_2 .^a

Entry	Substrate	Product	Conversion (mol%)	Selectivity (mol%)
1 ^b			2	99
2 ^c			7	99
3			99	99
4			97	99
5			91	99
6			99	99
7			98	99
8			93	99
9			98	99
10			98	99
11			99	42
				57
12 ^d			84	56
				43
13 ^e			66	62
				37

^a Reaction conditions: 1 mmol alcohol; 5 mmol (30% aq.) H_2O_2 ; 8 μ mol catalyst; 3 ml 1,4-dioxane; reaction temperature: 85 °C; reaction time: 7 h. The conversion was based on alcohols, the selectivity was based on ketone, aldehyde or acid. Conversions and selectivities were determined by gas chromatography using an internal standard technique.

^b No H_2O_2 .

^c No catalyst.

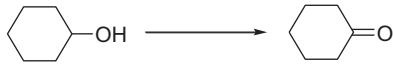

^d 1 mmol alcohol; 2 mmol (30% aq.) H_2O_2 .

^e 1 mmol alcohol; 1.5 mmol (30% aq.) H_2O_2 .

ondary alcohol (α -phenylethyl alcohol). In some reported systems, the solid alcohols were difficult to oxidize due to physiochemical considerations [35]. However, the solid alcohols of DL-menthol and benzhydrol were oxidized in high yields in this catalytic system. The above results show that this temperature-controlled phase transfer catalytic system is capable of catalytic activity for different kinds of secondary alcohols (hydrophilic alcohols, hydrophobic alcohols and solid alcohols). For primary alcohol, the

products in the oxidation of benzyl alcohol were benzaldehyde and benzoic acid. The oxidations of benzyl alcohol based on this catalytic system with different molar ratios of H_2O_2 /benzyl alcohol were investigated in detail. With increasing H_2O_2 /substrate molar ratio, the conversion of benzyl alcohol increased accordingly, but the selectivity of benzaldehyde decreased. It was found that the amount of hydrogen peroxide could affect the activity and selectivity in the oxidation of benzyl alcohol in this oxidation

Table 5
Oxidation of cyclohexanol and 2-octanol for different cycles.^a

					
Cycle	Conversion (mol%)	Selectivity (mol%)	Cycle	Conversion (mol%)	Selectivity (mol%)
1st use	99	99	1st use	93	99
2nd use	98	99	2nd use	91	99
3rd use	98	99	3rd use	91	99

^a Reaction conditions: 4 mmol alcohol; 20 mmol (30% aq.) H₂O₂; 32 μmol catalyst; 12 ml 1,4-dioxane; reaction temperature: 85 °C; reaction time: 7 h.

Table 6
Oxidation of 2-octanol under different solvents based on the catalyst.^a

Entry	Solvent	Solubility of catalyst		Conversion (mol%)	Selectivity (mol%)
		During reaction	After reaction		
1	1,4-Dioxane	Soluble	Insoluble	93	99
2	Toluene	Soluble	Soluble	91	99
3	Acetonitrile	Soluble	Insoluble	96	99
4	1,2-Dichloroethane	Soluble	Soluble	69	99
5	Ethyl acetate	Soluble	Insoluble	67	99

^a Reaction conditions: 1 mmol alcohol; 5 mmol (30% aq.) H₂O₂; 8 μmol catalyst; 3 ml solvent; reaction temperature: 85 °C; reaction time: 7 h.

system. Increasing amount of hydrogen peroxide enhanced the activity of oxidation, but the excess of oxidant promoted the deep oxidation, which would produce more benzoic acid.

The catalyst could be also easily recycled in this system. At the beginning of the reaction, the catalyst was insoluble in the solvent of 1,4-dioxane at room temperature. When the oxidation was carried out with heating, the catalyst dissolved in the system gradually. After the reaction finished with the temperature dropping, the system gradually changed from clear to turbid and the catalyst precipitated by itself from the system. The catalyst could be separated from the system by centrifugation and used for the next cycle. Table 5 lists the catalytic activity in oxidation of cyclohexanol and 2-octanol based on [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉] for different cycles. As shown in the table, the catalytic activity and selectivity of the recovered catalyst were the same as those of the fresh catalyst. For cyclic alcohol of cyclohexanol, after three cycles, a 97% yield of cyclohexanone with 99% selectivity was obtained. For linear aliphatic alcohol of 2-octanol, a 90% yield of octanone with 99% selectivity was still kept, indicating the excellent and stable activity of the catalyst.

The oxidation of 2-octanol under different solvents was investigated and shown in Table 6, several trends may be noted. The catalyst was all soluble in these solvents during the reaction. However, after the oxidation with temperature dropping, the catalyst precipitated from the system in 1,4-dioxane, acetonitrile and ethyl acetate, but dissolved in toluene and 1,2-dichloroethane. The polarity of 1,4-dioxane, acetonitrile and ethyl acetate is stronger than that of toluene and 1,2-dichloroethane. So we presume that the strong polarity of solvent may be helpful for the property of temperature-controlled phase transfer catalysis. Compared to the activity of the catalyst in oxidation of 2-octanol during the polar solvents, high conversion of 93% and 96% was obtained in acetonitrile and 1,4-dioxane, respectively. Considering the strong toxicity of acetonitrile, 1,4-dioxane was chosen as the best solvent in this system from the viewpoint of green chemistry.

The solubility of the catalyst in the reaction solution for the oxidation of cyclohexanol was determined during different temperatures (Table 7). From 20 °C to 45 °C, the catalyst was insoluble in the system. When the reaction temperature reached 48 °C, the catalyst started to dissolve. The system became clear gradually with heating continually, and the catalyst was dissolved completely at 53 °C. The catalyst was always soluble in the solution at 55–85 °C. To well prove that this system indeed has the charac-

ter of temperature-controlled phase transfer catalysis, the effect of temperature on the solubility of catalyst in the oxidation is shown in Table 8. The catalyst was insoluble in 1,4-dioxane without substrate and H₂O₂ at room temperature (entry 1). But it dissolved gradually in the solvent after heating and precipitated from the system with cooling. The catalyst could effectively oxidize substrates in a homogeneous system and easily be recycled by changing the temperature. This catalytic system is very different from the reaction-controlled phase transfer catalytic systems which were reported before [27,28,42]. In that system, when the deficient H₂O₂ was consumed up, the catalyst could be recovered from the reaction system by centrifugation. However, the important factor for the recovery of the catalyst in our system is not the H₂O₂ but the temperature. As shown in the table, the amount of H₂O₂ was added from 1 mmol to 10 mmol; the catalyst could precipitate in any case from the solvent after the reaction with the temperature dropping. Whether the olefin was added or not, and whether the H₂O₂ was equivalent or excessive, the catalyst all had the temperature-controlled phase transfer characters. The results proved that this system is indeed a temperature-controlled phase transfer catalytic system.

The fresh catalyst and recovered catalysts were characterized with FT-IR spectra and ³¹P MAS NMR. As shown in Fig. 2, the IR

Table 7
Solubility of the catalyst in the reaction solution under different temperatures.^a

Entry	Temperature (°C)	Solubility
1	20	Insoluble
2	25	Insoluble
3	30	Insoluble
4	35	Insoluble
5	40	Insoluble
6	42	Insoluble
7	45	Insoluble
8	48	Start dissolving
9	53	Dissolved completely
10	55	Soluble
11	60	Soluble
12	65	Soluble
13	70	Soluble
14	80	Soluble
15	85	Soluble

^a Reaction conditions: 1 mmol cyclohexanol; 5 mmol (30% aq.) H₂O₂; 8 μmol catalyst; 3 ml 1,4-dioxane; reaction temperature: 20–85 °C.

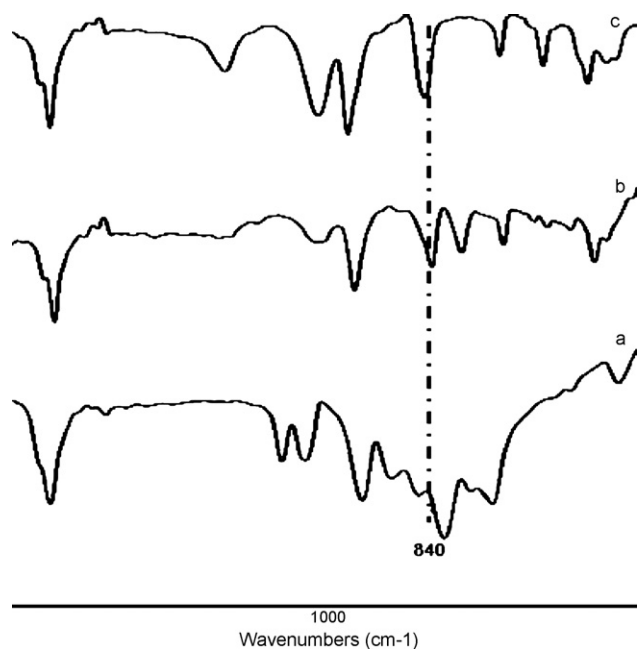
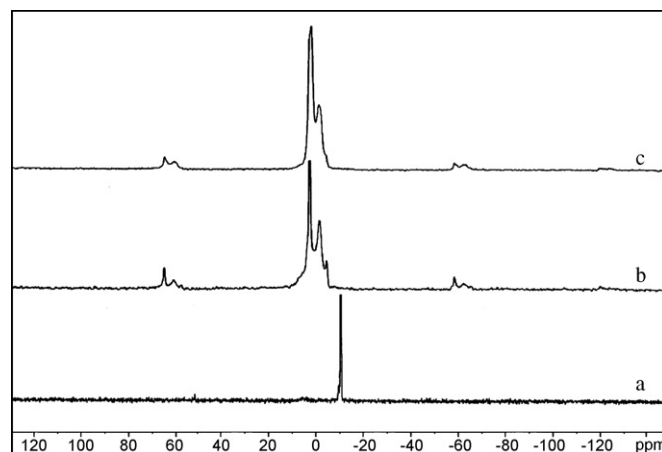
Table 8
The effect of temperature on the solubility of catalyst.^a

Entry	Cyclohexanol	H ₂ O ₂	Room temperature 20 °C	High temperature 85 °C	Low temperature ≤20 °C
1	0	0	Insoluble	Soluble	Insoluble
2	1	0	Insoluble	Soluble	Insoluble
3	1	1	Insoluble	Soluble	Insoluble
4	1	5	Insoluble	Soluble	Insoluble
5	1	10	Insoluble	Soluble	Insoluble

^a Experimental conditions: 8 μmol catalyst, 3 ml 1,4-dioxane with vigorous stirring.

spectrum of the fresh catalyst exhibited characteristic peaks at 1079–1040, 945 and 900–725 cm⁻¹ which were attributed to ν (P–O), ν (W=O) and ν (W–O–W), respectively [43]. There were some differences between the IR spectrum of the fresh catalyst and the first used one. An obvious peak at 840 cm⁻¹ was appeared for the latter, which was attributed to ν (O–O) [44]. There was also a strong peak at 844 cm⁻¹ in the IR spectrum of the catalyst of cycle 2, which was similar with the catalyst of cycle 1. The ³¹P MAS NMR spectra of the catalysts are shown in Fig. 3. A single peak at –10.2 ppm is shown in Fig. 1a, it should be attributed to the lacunary structure of [PW₁₁O₃₉]⁷⁻ [45]. The spectrum of the used catalyst (Fig. 3b) shows several broad peaks and suggests that the catalyst is a mixture that contains several different polytungstophosphate species. The main peak at 2.7 ppm can be attributed to active tungsten-peroxo complex, which is consistent with the IR spectrum. The peaks at –1.6 and –4.6 ppm should be other low W/P polytungstophosphate species. The ³¹P MAS NMR spectrum of the catalyst of cycle 2 (Fig. 3c) was similar to that of cycle 1, indicating that the structure of the pre-catalyst would not change from the first cycle.

According to the above characterization results, we proposed a possible mechanism for the oxidation of alcohols in this temperature-controlled phase transfer catalysis system. When the reaction was heated and H₂O₂ was added to the solution of catalyst, the fresh structure of [PW₁₁O₃₉]⁷⁻ became a mixture of polytungstophosphate species. These species could be exchanged to each other in solution, and finally formed the peroxo tungstophosphate intermediate, which was active and responsible for the oxidation. After the oxidation finished, the catalyst changed back

**Fig. 2.** IR spectra of: (a) the fresh catalyst of [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉]; (b) the catalyst of cycle 1; (c) the catalyst of cycle 2.**Fig. 3.** ³¹P MAS NMR spectra of: (a) the fresh catalyst of [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉]; (b) the catalyst of cycle 1; (c) the catalyst of cycle 2.

to the mixture of polytungstophosphate species. These species have the temperature-controlled phase transfer property under the effect of unique solvent and the special big cation, and can be recycled for the oxidation without changes of structure.

4. Conclusions

In summary, a recyclable, effective, and stable catalytic system has been developed for the oxidation of pyridines and alcohols to the corresponding N-oxides and ketones based on a temperature-controlled phase transfer catalyst of [(C₁₈H₃₇)₂(CH₃)₂N]₇[PW₁₁O₃₉]. High to excellent yields were achieved. After reaction with cooling, the catalyst precipitated from the system and could be recovered by centrifugation as deposit. There was no discernible loss in activity or selectivity after several cycles.

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References

- [1] A. Albini, *Synthesis* (1993) 263–277.
- [2] A.V. Malkov, M. Bell, F. Castelluzzo, P. Kočovský, *Org. Lett.* 7 (2005) 3219–3222.
- [3] L.-C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* 127 (2005) 18020–18021.
- [4] R. Sarma, A. Karmakar, J.B. Baruah, *Inorg. Chim. Acta* 361 (2008) 2081–2086.
- [5] H.S. Mosher, L. Turner, A. Carlsmith, *Org. Synth. Coll. Vol. IV* (1963) 828–830.
- [6] J.G. Robbe, E.J. Behrman, *J. Chem. Res. S* (1993) 412–413.
- [7] M. Ferrer, F. Sanchez-Baeza, A. Messgure, *Tetrahedron* 53 (1997) 15877–15888.
- [8] P. Brougham, M.S. Cooper, D.A. Cummerson, H. Heaney, N. Thomson, *Synthesis* (1987) 1015–1017.
- [9] V. Boekelheide, W.J. Linn, *J. Am. Chem. Soc.* 76 (1954) 1286–1291.
- [10] C. Copéret, H. Adolffson, T.V. Khuong, A.K. Yudin, K.B. Sharpless, *J. Org. Chem.* 63 (1998) 1740–1741.

- [11] D. Rong, V.A. Phillips, R.S. Rubio, M. Castro, R.T. Wheelhouse, *Tetrahedron Lett.* 49 (2008) 6933–6935.
- [12] X.Z. Zhu, K.D. Kreutter, H.P. Hu, M.R. Player, M.D. Gaul, *Tetrahedron Lett.* 49 (2008) 832–834.
- [13] K. Neimann, R. Neumann, *Chem. Commun.* (2001) 487–488.
- [14] D.J. Robinson, P. McMorn, D. Bethell, P.C. Bulman-Page, C. Slyd, F. King, F.E. Hancock, G.J. Hutchings, *Catal. Lett.* 72 (2001) 233–234.
- [15] L. Rout, T. Punniyamurthy, *Adv. Synth. Catal.* 347 (2005) 1958–1960.
- [16] T. Fey, H. Fischer, S. Bachmann, K. Albert, C. Bolm, *J. Org. Chem.* 66 (2001) 8154–8159.
- [17] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, *Catal. Today* 57 (2000) 157–166.
- [18] R.P. Singh, H.N. Subbarao, S. Dev, *Tetrahedron* 35 (1979) 1789–1793.
- [19] C. Venturello, M. Gambaro, *J. Org. Chem.* 56 (1991) 5924–5931.
- [20] Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, *J. Org. Chem.* 52 (1987) 1868–1870.
- [21] Y. Ishi, H. Tanaka, Y. Nisiyama, *Chem. Lett.* (1994) 1–4.
- [22] M. Carraro, L. Sandei, A. Sartorel, G. Scorrano, M. Bonchio, *Org. Lett.* 8 (2006) 3671–3674.
- [23] K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng, R. Noyori, *Tetrahedron* 57 (2001) 2469–2476.
- [24] F.F. Bamoharram, M. Roshani, M.M. Heravi, S. Safaie, *Phosphorus Sulfur Silicon Relat. Elem.* 181 (2006) 2833–2841.
- [25] P. Tundo, G.P. Romanelli, P.G. Vázquez, F. Aricò, *Catal. Commun.* 11 (2010) 1181–1184.
- [26] S.J. Zhang, G.D. Zhao, S. Gao, Z.W. Xi, J. Xu, *J. Mol. Catal. A: Chem.* 289 (2008) 22–27.
- [27] S.J. Zhang, S. Gao, Z.W. Xi, J. Xu, *Catal. Commun.* 8 (2007) 531–534.
- [28] Z.H. Weng, J.Y. Wang, X.G. Jian, *Catal. Commun.* 9 (2008) 1688–1691.
- [29] G.J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636–1639.
- [30] D. Sloboda-Rozner, P.L. Alsters, R. Neumann, *J. Am. Chem. Soc.* 125 (2003) 5280–5281.
- [31] J.M. Wang, L. Yan, G.X. Li, X.L. Wang, Y. Ding, J.S. Suo, *Tetrahedron Lett.* 46 (2005) 7023–7027.
- [32] B.C. Ma, Y.S. Zhang, Y. Ding, W. Zhao, *Catal. Commun.* 11 (2010) 853–857.
- [33] W. Zhao, Y.S. Zhang, B.C. Ma, Y. Ding, W.Y. Qiu, *Catal. Commun.* 11 (2010) 527–531.
- [34] J.M. Wang, L. Yan, G. Qian, S.Q. Li, K.L. Yang, H.T. Liu, X.L. Wang, *Tetrahedron* 63 (2007) 1826–1832.
- [35] D. Sloboda-Rozner, P. Witte, P.L. Alsters, R. Neumann, *Adv. Synth. Catal.* 346 (2004) 339–345.
- [36] H. Hamamoto, Y. Suzuki, Y.M.A. Yamada, H. Tabata, H. Takahashi, S. Ikegami, *Angew. Chem. Int. Ed.* 44 (2005) 4536–4538.
- [37] Z.H. Weng, J.Y. Wang, S.H. Zhang, C. Yan, X.G. Jian, *Catal. Commun.* 10 (2008) 125–128.
- [38] M.V. Vasylyev, R. Neumann, *J. Am. Chem. Soc.* 126 (2004) 884–890.
- [39] A. Behr, B. Turkowski, R. Roll, R. Schöbel, G. Henze, *Top. Organomet. Chem.* 23 (2008) 19–52.
- [40] J.A. Gladysz, V. Tesevic, *Top. Organomet. Chem.* 23 (2008) 67–89.
- [41] R.G. Finke, M.W. Droege, P.J. Dommille, *Inorg. Chem.* 26 (1987) 3886–3896.
- [42] Z.W. Xi, N. Zhou, Y. Sun, K.L. Li, *Science* 292 (2001) 1139–1141.
- [43] E. Radkov, R.H. Beer, *Polyhedron* 15–16 (14) (1995) 2139–2143.
- [44] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553–1557.
- [45] R. Massart, R. Contant, J.M. Fruchart, J.P. Ciabrini, M. Fournier, *Inorg. Chem.* 16 (1977) 2916–2921.