ORIGINAL PAPER

# Efficient and convenient oxidation of alcohols to aldehydes and ketones with $H_2O_2/(NH_4)_6Mo_7O_{24}.4H_2O$ regulated by PEG<sub>1000</sub>-DIL/methylcyclohexane temperature-dependent biphasic system

Yu-Lin Hu · Ming Lu · Xiu-Tao Ge

Received: 13 July 2012/Accepted: 3 October 2012/Published online: 17 January 2013 © Iranian Chemical Society 2013

**Abstract** A simple and efficient method for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with  $H_2O_2/(NH4)_6Mo_7O_{24}.4H_2O$ using the PEG<sub>1000</sub>-DIL/methylcyclohexane temperaturedependent biphasic system has been developed. The product can be easily isolated by a simple decantation, and the catalytic system can be recycled or reused without loss of catalytic activity.

### Introduction

Aldehydes and ketones are important classes of chemicals that have been used extensively as synthetic intermediates in the preparation of a variety of fine or special chemicals such as drugs, vitamins, fragrances, etc. [1]. Up to now, many publications in the open literature have been found in synthesis of these type of compounds, and a well-known method for such a synthesis constitutes the oxidation of alcohols [2]. Traditional methods for performing such a transformation generally involve the use of stoichiometric amount of the strongest oxidizing reagents (i.e., KMnO<sub>4</sub>,

Y.-L. Hu (🖂) · X.-T. Ge

College of Material Science and Chemical Engineering, Chuzhou University, Chuzhou 239000, People's Republic of China e-mail: huyulin1982@163.com

M. Lu

MnO<sub>2</sub>, CrO<sub>3</sub>, SeO<sub>2</sub>, Br<sub>2</sub>, RuO<sub>4</sub>, etc.) [3–5]. However, these protocols are generally associated with one or more disadvantages, such as high cost, low yield, harsh or delicate reaction conditions, and a large amount of waste byproducts. Aerobic oxidation of alcohols using transition metal complexes as catalysts is another important method for this transformation, and a variety of reagents, such as cobalt [6, 7], copper [8–10], gold [11], nickel [12], iron [13], osmium [14, 15], palladium [16–18], ruthenium [19, 20], molybdenum [21], vanadium [22, 23], and other complexes [24–26], have been developed with different degrees of success. However, most of the procedures still suffered from the use of expensive reagents, difficulties in work up, environmental hazards, and difficulties in recycling of the catalyst. Besides molecular oxygen, hydrogen peroxide  $(H_2O_2)$  is an another environmentally friendly and atom-efficient oxidant which leads to only water after the reaction [27]. This reagent has, however, high activation energy, making catalysis necessary [28], and a number of catalytic oxidation processes based upon the combination of transition metals or organocatalysts have been developed for such a conversion [29–32]. However, most of these methods are invariably suffered from limitations such as lower yields, poor recovery of expensive metal catalysts and laborious workup procedures. Consequently, there is a great need to develop new and environment-benign procedures that address these drawbacks for such a conversion.

Ionic liquids (ILs) have recently gained recognition as environmentally benign alternative solvents, because of their favorable properties such as negligible volatility and nonflammability under ambient conditions, large liquid range, high thermal stability, wide electrochemical window, and strong ability to dissolve many chemicals [33]. Therefore, ILs have found wide applications in chemical synthesis [34–36], biocatalytic transformations [37], electrochemistry

College of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

Scheme 1 Oxidation of alcohols and synthesis of PEG<sub>1000</sub>-DIL. Reagents and conditions: (i) toluene, triethylamine (2 equiv.), CH<sub>3</sub>SO<sub>2</sub>Cl (2 equiv.), 30 °C, 4 h. (ii) toluene, methyl imidazole (2 equiv.), 80 °C, 18 h



3

[38], and analytical and separation science [39]. In view of both the advantages and disadvantages of homogeneous and heterogeneous catalysts, and to improve catalyst recovery, multiphase systems, such as phase-transfer catalysis [40, 41], thermoregulated phase transfer catalysis [42], and liquidliquid biphasic catalysis [43], have been studied. Some novel temperature-dependent ionic liquid biphasic catalytic systems have been reported recently [44-47], and found that these temperature-dependent ILs showed some advantages such as high conversions and selectivity, stability at high temperatures, easy handling and separation, excellent reusability in the reaction, etc., which provide a novel route for the homogeneous catalysis and the separation and recycling of catalysts. In 2009, we developed an efficient synthetic method for the dichloromethylation of some aromatic hydrocarbons in [C<sub>12</sub>minPEG<sub>800</sub>]Br/methylcyclohexane temperature-dependent phase-separation system in aqueous media [48]. Based on the concept of thermoregulated ionic liquid biphasic system (TRILC) and in continuation of our interest in exploring green synthetic methods using ionic liquids, we herein report an efficient and convenient procedure for the oxidation of primary and secondary alcohols to the aldehydes and ketones using aqueous H<sub>2</sub>O<sub>2</sub> as oxidant and ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O) as the catalyst in the PEG<sub>1000</sub>-based dicationic ionic liquid  $(PEG_{1000}$ -DIL) (Scheme 1).

# Experimental

#### Apparatus and reagents

All the used chemicals were from commercial sources without any pretreatment. All reagents were of analytical

grade. The ionic liquid was synthesized according to the literature procedure [47, 48]. High performance liquid chromatography (HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America), consisting of a pump (P680) and ultraviolet–visible light detector (UVD) system (170U). The experiments were performed on discovery C18 column,  $\phi$  4.6 × 250 mm. <sup>1</sup>H NMR spectra were recorded on a Bruker 400-MHz spectrometer using CDCl<sub>3</sub> as the solvent with tetramethylsilane (TMS) as an internal standard. The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. Mass spectra were measured on an HP1100LC (Agilent Technologies, USA). Elemental analysis was performed on a Vario EL III instrument (Elmentar Anlalysensy Teme GmbH, Germany).

Typical procedure for the preparation of ionic liquid  $PEG_{1000}$ -DIL

(1) Preparation of intermediate **2**: a mixture of PEG-1000 (**1**, 0.1 mol), triethylamine (0.2 mol), and toluene (300 mL) was stirred in 500 mL round flask at 0–5 °C, then  $CH_3SO_2$ Cl (0.2 mol) was added dropwise slowly, after that the mixture was stirred for another 4 h at 30 °C. The reaction progress was monitored by TLC and HPLC. Upon completion, the mixture was cooled to 10 °C, the organic phase (top layer) was appeared and then separated by decantation, the bottom layer was extracted with toluene (2 × 10 mL). The combined organic phases were the toluene solvent of **2**. (2) Preparation of ionic liquid PEG<sub>1000</sub>-DIL **3**: methyl imidazole (0.2 mol) was added dropwise into the toluene solvent of intermediate **2** at room temperature, with vigorous stirring, then the mixture was stirred for another 18 h at 80 °C. The reaction progress was monitored by HPLC and <sup>1</sup>H NMR. After the reaction completed, the mixture was cooled, the solvent was recovered under reduced pressure to give  $PEG_{1000}$ -DIL as a viscous yellowish-brown liquid, yield 85 %.

Intermediate **2** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.1 (s, 6H, CH<sub>3</sub> × 2), 3.65–3.80 (m, 92H, (OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>), 4.39–4.43 (t, 4H, CH<sub>2</sub> × 2) ppm.

PEG<sub>1000</sub>-DIL <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.76 (s, 6H, CH<sub>3</sub> × 2), 3.58–3.73 (m, 92H, (OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>), 4.03 (s, 6H, NCH<sub>3</sub> × 2), 4.57 (t, 4H, CH<sub>2</sub> × 2), 7.34 (s, 4H, CH × 4), 7.69 (s, 2H, CH × 2) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 36.3, 39.7, 49.3, 69.1, 70.2, 70.5, 123.4, 137.4, 137.7 ppm. IR (KBr, cm<sup>-1</sup>): 627, 772, 854, 1108, 1321, 1410, 1457, 1528, 1837, 2876, 3105, 3445. MS (EI, 70 eV) m/z (%): 448, 470, 492, 514, 558, 580, 602, 624, 646, 668, 690, 712, 153 (100).

General procedure for oxidation reaction

To a stirred solution of alcohol (10 mmol) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>  $O_{24}.4H_2O\left(6\,\text{ mmol}\right)$  in ionic liquid  $PEG_{1000}\text{-}DIL\left(5\,\text{ mL}\right)$  and methylcyclohexane (10 mL) was added aqueous H<sub>2</sub>O<sub>2</sub> (30 %, 10 mL) at room temperature. The reaction mixture was stirred at 50 °C for the appropriate time (Table 2), the progress of the reaction was monitored by HPLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and the organic phase was separated by decantation, and then rinsed with water  $(3 \times 10 \text{ mL})$ . The organic phase was dried with sodium sulfate, filtered, and the solvent was removed, and the residue was passed through a silica gel pad to afford the pure product. The next run was performed under identical reaction conditions. All the products are known compounds and their structures were characterized by elemental analysis, <sup>1</sup>H NMR or compared with their authentic samples. The physical and spectral data of the products are given below.

Benzaldehyde (Table 2, entry 1) Colorless oil, bp 178–179 °C/760 mm (lit. 178–180 °C/760 mm) [49–52].

2-Methylbenzaldehyde (Table 2, entry 2) Colorless oil, bp 200–202 °C/760 mm (lit. 199–200 °C/760 mm) [49–52].

4-Methoxybenzaldehyde (Table 2, entry 3) Colorless oil, bp 246–247 °C/760 mm (lit. 248–250 °C/760 mm) [49– 52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.89 (s, 3H, CH<sub>3</sub>O), 7.02 (m, 2H, Ar–H), 7.86 (m, 2H, Ar–H), 9.96 (s, 1H, CHO) ppm. Anal. Calcd. for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>: C, 70.53; H, 5.94; O, 23.47. Found: C, 70.57; H, 5.92; O, 23.50.

4-Tert-butylbenzaldehyde (Table 2, entry 4) Colorless oil, bp 128–129 °C/25 mm (lit. 130–132 °C/25 mm) [49–52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.31 (s, CH<sub>3</sub>, 9H), 7.53–7.79 (m, Ar–H, 4H), 9.96 (s, CHO, 1H) ppm. Anal.

Calcd. for C<sub>11</sub>H<sub>14</sub>O: C, 81.38; H, 8.71; O, 9.85. Found: C, 81.44; H, 8.70; O, 9.86.

3,4,5-Trimethoxybenzaldehyde (Table 2, entry 5) White solid, mp 74–76 °C (lit. 75–78 °C) [49–52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.87 (s, 3H, CH<sub>3</sub>O), 7.16 (s, 2H, Ar–H), 9.89 (s, 1H, CHO) ppm. Anal. Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>: C, 61.21; H, 6.14; O, 32.61. Found: C, 61.22; H, 6.16; O, 32.62.

3,4-(Methylenedioxy)benzaldehyde (Table 2, entry 6) White solid, mp 36–38 °C (lit. 35–36 °C) [49–52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.04$  (s, CH<sub>2</sub>, 2H), 6.86–7.53 (m, Ar–H, 3H), 9.86 (s, CHO, 1H) ppm. Anal. Calcd for C<sub>8</sub>H<sub>6</sub>O<sub>3</sub>: C, 63.99; H, 4.01; O, 31.98. Found: C, 64.00; H, 4.03; O, 31.97.

4-Fluorobenzaldehyde (Table 2, entry 7) Colorless oil, bp 180–182 °C/760 mm (lit. 181–183 °C/760 mm) [49–52].

4-Nitrobenzaldehyde (Table 2, entry 8) Light yellow solid, mp 104–106 °C (lit. 106–107 °C) [49–52].

2-Hydroxy-1-phenylethanone (Table 2, entry 9) White solid, mp 86–87 °C (lit. 87–90 °C) [49–52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.78 (s, OH, 1H), 4.67 (s, CH<sub>2</sub>, 2H), 7.52–7.61 (m, Ar–H, 3H), 7.79–7.83 (m, Ar–H, 2H) ppm. Anal. Calcd for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>: C, 70.53; H, 5.89; O, 23.47. Found: C, 70.57; H, 5.92; O, 23.50.

Acetophenone (Table 2, entry 10) White solid, mp  $18-19 \degree C$  (lit.  $19-20 \degree C$ ) [49-52].

trans-Cinnamaldehyde (Table 2, entry 11) Colorless oil, bp 247–249 °C/760 mm (lit. 251–252 °C/760 mm) [49–52]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.65$  (d, J = 16.7 Hz, CH, 1H), 6.69 (dd, J = 6.5, 16.7 Hz, CH, 1H), 7.36–7.51 (m, Ar–H, 5H), 9.65 (d, J = 6.5 Hz, CHO, 1H) ppm. Anal. Calcd for C<sub>9</sub>H<sub>8</sub>O: C, 81.79; H, 6.10; O, 12.11. Found: C, 81.79; H, 6.10; O, 12.11.

3,7-Dimethyl-2,6-octadienal (Table 2, entry 12) Colorless oil, bp 227–230 °C/760 mm (lit. 229–232 °C/ 760 mm) [49–52].

3-Phenylpropanal (Table 2, entry 13) White solid, mp 45-47 °C (lit. 47-48 °C) [49-52].

Hexanal (Table 2, entry 14) Colorless oil, bp 126–129 °C/760 mm (lit. 128–130 °C/760 mm) [49–52].

Cyclohexanone (Table 2, entry 15) Colorless oil, bp 157–160 °C/760 mm (lit. 156–158 °C/760 mm) [49–52].

#### **Results and discussion**

The initial study was carried out using 4-methoxybenzyl alcohol as the substrate to optimize the reaction conditions,

**Table 1** Optimization of the reaction conditions for oxidizing

 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde

Entry <sup>a</sup>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> .4H <sub>2</sub> O (equiv.)	Time (h)	Yield (%) <sup>b</sup>	
1	-	8	68	
2	0.1	4	77	
3	0.3	3	86	
4	0.5	2	92	
5	0.6	2	95	
6	0.7	2	95	
7	0.6	5 <sup>c</sup>	74	

 $^a$  Reaction conditions: 4-methoxybenzyl alcohol (10 mmol), H\_2O\_2 (30 %, 10 mL), PEG\_{1000}\text{-DIL} (5 mL), methylcyclohexane (10 mL), 50 °C

<sup>b</sup> Isolated yield

 $^{c}$  Reaction was carried out in the absence of the PEG<sub>1000</sub>-DIL/ methylcyclohexane biphasic system

and the results are summarized in Table 1. The oxidation with 30 % H<sub>2</sub>O<sub>2</sub> was investigated first in the presence and absence of the catalyst (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (Table 1). 4-Methoxybenzyl alcohol was oxidized with  $H_2O_2$  in the absence of the catalyst to produce the 4-methoxybenzaldehyde; however, the reaction proceeded slowly, the yield was only 68 % after 8 h (Table 1, entry 1). When the oxidation was catalyzed by (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O, the yield increased to 77 % in a shorter time (4 h) when only 0.1 equiv. was used (Table 1, entry 2). The yield increased with the increase in the amount of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (Table 1, entries 2-5), and it reached maximum when 0.6 equiv. of the catalyst was used (Table 1, entry 5). However, on further addition of the amount of  $(NH_4)_6$ Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O, the yield was not enhanced significantly (Table 1, entry 6). In addition, the PEG<sub>1000</sub>-DIL/methylcyclohexane temperature-dependent biphasic system is crucial for this oxidation, and the lack of it leads to a lower yield and a slower reaction rate (Table 1, entry 7). Furthermore, no over-oxidized product (4-methoxybenzoic acid) was detected by HPLC analysis of the crude reaction mixtures in all the cases.

Figure 1 shows the influences of reaction temperature on the oxidation. The catalytic activity increased with the temperature to 50 °C; however, the yield was decreased with the further increase of the temperature, which is due to the formation of the over-oxidized product (4-methoxybenzoic acid), which was confirmed by HPLC. The yield reached maximum at 50 °C, these results show that the moderate temperature, such as 50 °C enhanced the oxidation.

In addition, the catalytic system could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Fig. 2). The recycling process involved the removal of the upper



Fig. 1 Influences of temperature on the oxidation. Reaction conditions: 4-methoxybenzyl alcohol (10 mmol),  $H_2O_2$  (30 %, 10 mL), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (6 mmol), PEG<sub>1000</sub>-DIL (5 mL), methylcyclohexane (10 mL), 2 h

layer of methylcyclohexane (oil layer), containing product, by decantation and concentration of the under layer of catalytic system (aqueous layer) by removing the water through a water knockout drum. Fresh substrates and methylcyclohexane were then recharged to the recovered catalytic system and the mixture was heated to react once again.

With these results in hand, the catalytic system was then applied to various alcohols, as summarized in Table 2. It is clear that various types of benzylic, allylic and aliphatic alcohols, both primary and secondary, have been successfully oxidized to the corresponding aldehydes and ketones in good to high yields (Table 2). Various functionalities such as alkyl, alkoxy, alkene double bonds, fluoro, and nitro groups can tolerate the oxidation. However, the aliphatic alcohols were less reactive, and longer reaction time and elevated temperature were needed to reach good yields (Table 2, entries 13–15). It was also observed that the electron deficiency and nature of the substituents on the aromatic ring have influence on the oxidation rate, and benzylic alcohols



Fig. 2 Repeating reactions using recovered catalytic system. Reaction conditions: 4-methoxybenzyl alcohol (10 mmol),  $H_2O_2$  (30 %, 10 mL), methylcyclohexane (10 mL), recovered catalytic system (PEG<sub>1000</sub>-DIL and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O), 50 °C, 2 h

to aldehydes and ketones

Entry <sup>a</sup>	Substrate	Product <sup>b</sup>	Time (h)	Yield $(\%)^{c}$
1	CH <sub>2</sub> OH	СНО	3	94
2	CH <sub>2</sub> OH	H <sub>3</sub> C	2	93
3	CH <sub>2</sub> OH	CHO OCH <sub>3</sub>	2	95
4	CH <sub>2</sub> OH C(CH <sub>3</sub> ) <sub>3</sub>	CHO C(CH <sub>3</sub> ) <sub>3</sub>	2	94
5	H <sub>3</sub> CO OCH <sub>3</sub>	H <sub>3</sub> CO OCH <sub>3</sub>	2	97
6	O CH <sub>2</sub> OH	О СНО	2	96
7	CH <sub>2</sub> OH	CHO	4	94
8	CH <sub>2</sub> OH	CHO NO <sub>2</sub>	4	92
9	ОНОН	ОН	2	93
10	CH <sub>3</sub>	CH3	2	94

# Table 2 continued

	Entry <sup>a</sup>	Substrate	Product <sup>b</sup>	Time (h)	Yield $(\%)^c$
	11	ОН	СНО	2	96
<sup>a</sup> Reaction conditions: alcohol (10 mmol), $H_2O_2$ (30 %, 41 O	12	ОН	СНО	2	97
10 mL), $(NH_4)_6Mo_7O_{24}.4H_2O$ (6 mmol), $PEG_{1000}$ -DIL (5 mL), methylcyclohexane (10 mL), 50 °C	13	ОН	СНО	5 <sup>d</sup>	90
<sup>b</sup> All products were known and identified by comparing their	14	ОН	СНО	5 <sup>d</sup>	85
HPLC spectra with those of commercial materials	15	он	o ↓	حط	00
<sup>c</sup> Isolated yield	15			5	88
<sup>d</sup> The reaction was carried out at 70 °C		$\checkmark$	$\checkmark$		

having electron-withdrawing groups on the aromatic ring (Table 2, entries 7, 8) exerted a little inactivation for the reaction contrast to those having electron-donating groups (Table 2, entries 2-6). Obviously, the PEG<sub>1000</sub>-DIL/ (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O catalytic system was found to be more effective in oxidation of benzylic and allylic alcohols than that of aliphatic alcohols, which might be attributed to the different reaction abilities of  $\alpha$ -carbon groups when in the oxidation of benzylic, allylic and aliphatic alcohols with  $H_2O_2$  (oxidant). The reaction rate of oxidation depended on what was being oxidated, under the same conditions, the substrate molecule which contained better abilities of  $\alpha$ -carbon groups (e.g., benzylic and allylic alcohols) would lead to a much easier reaction attack, and a faster reaction rate and a higher yield were obtained.

The excellent reaction results of the catalytic system suggest that the oxidation among alcohols,  $H_2O_2$ ,  $(NH_4)_6$ Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O, methylcyclohexane and PEG<sub>1000</sub>-DIL has a particular catalytic process, which is schematically depicted in Fig. 3. Before the oxidation, there exists an obvious oil-water biphasic system, and the under layer (aqueous phase) consists of PEG<sub>1000</sub>-DIL, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, and PEG<sub>1000</sub>-DIL is dissolved completely in the aqueous medium, the upper layer (oil phase) consists of methylcyclohexane and alcohols (substrates). During the process of oxidation, the oil-water biphasic system disappears and a homogeneous reaction medium is formed, and the oxidation proceeds homogeneously. After the completion of the reaction, a complete phase-separation is formed again after being cooled to room temperature, the next



#### Fig. 3 Thermoregulated ionic liquid biphase catalytic process for the oxidation

process involved the removal of the upper layer of methylcyclohexane (oil layer), containing product, by decantation and concentration of the under layer of catalytic system (aqueous layer) by removing the water through a water knockout drum. Fresh substrates and methylcyclohexane were then recharged to the residual  $PEG_{1000}$ -DIL and  $(NH_4)_6Mo_7O_{24}.4H_2O$  and then recycled. The  $PEG_{1000}$ -DIL plays a very important role in the oxidation process to locally concentrate the reacting species near them by exhibiting a temperature-dependent phase behavior with methylcyclohexane (i.e., the thermoregulated biphasic behavior of mono-phase under high temperature and bi-phase under room temperature), which leads to a large increase in the effective reactant concentration and the excellent results of oxidation.

## Conclusion

In conclusion, we have developed an efficient method for oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with  $H_2O_2/(NH_4)_6$  $Mo_7O_{24}.4H_2O$  using the PEG<sub>1000</sub>-DIL/methylcyclohexane temperature-dependent biphasic system. Mild reaction conditions, easy workup, high yields, stability, easy isolation of the compounds, good thermoregulated biphasic behavior of the IL, and excellent recyclability of the catalytic system are the attractive features of this methodology. Further aspects of the catalysis and the application to other organic synthesis are under investigation.

**Acknowledgments** We thank the National Basic Research Program (973) of China and Natural Science Foundation of Jiangsu Province for support of this research.

#### References

- 1. T. Mallat, A. Baiker, Chem. Rev. 104, 3037 (2004)
- 2. M. Hudlick, *Oxidations in organic chemistry* (American Chemical Society, Washington, DC, 1990)
- 3. J. March, Advanced organic chemistry: reactions, mechanisms, and structure (John Wiley and Sons, New York, 1992)
- A. Ghorbani-Choghamarani, G. Azadi, J. Iran. Chem. Soc. 8, 1082 (2011)
- A.R. Hajipour, L. Khazdooz, A.E. Ruoho, J. Iran. Chem. Soc. 8, 382 (2011)
- 6. A.K. Mandal, J. Iqbal, Tetrahedron 53, 7641 (1997)
- V.B. Sharma, S.L. Jain, B. Sain, J. Mol. Catal. A: Chem. 212, 55 (2004)
- P. Chaudhuri, M. Hess, J. Mueller, K. Hildenbrand, E. Bill, T. Weyhermueller, K. Wieghardt, J. Am. Chem. Soc. **121**, 9599 (1999)
- I.E. Marko, P.R. Giles, M. Tsukazaki, R.I. Chelle, A. Gautier, S.M. Brown, C.J. Urch, J. Org. Chem. 64, 2433 (1999)

- P. Gamez, I.W.C.E. Arends, R.A. Sheldon, J. Reedijk, Adv. Synth. Catal. 346, 805 (2004)
- B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, J. Am. Chem. Soc. **127**, 18004 (2005)
- B.M. Choudary, M.L. Kantam, A. Rahman, C.V. Reddy, K.K. Rao, Angew. Chem. Int. Ed. 40, 763 (2001)
- N. Wang, R. Liu, J. Chen, X. Liang, Chem. Commun. 14(42), 5322–5324 (2005)
- C. Dobler, G.M. Mehltretter, U. Sundermeier, M. Eckert, H.C. Militzer, M. Beller, Tetrahedron Lett. 42, 8447 (2001)
- P.A. Shapley, N. Zhang, J.L. Allen, D.H. Pool, H.C. Liang, J. Am. Chem. Soc. **122**, 1079 (2000)
- N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, J. Org. Chem. 66, 662 (2001)
- 17. B.A. Steinhoff, S.S. Stahl, J. Am. Chem. Soc. 128, 4348 (2006)
- D.D. Caspi, D.C. Ebner, J.T. Bagdanoff, B.M. Stoltz, Adv. Synth. Catal. 346, 185 (2004)
- H. Shimizu, S. Onitsuka, H. Egami, T. Katsuki, J. Am. Chem. Soc. 127, 5396 (2005)
- 20. K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 41, 4538 (2002)
- 21. S. Velusamy, M. Ahamed, T. Punniyamurthy, Org. Lett. 6, 4821 (2004)
- 22. S. Velusamy, T. Punniyamurthy, Org. Lett. 6, 217 (2004)
- 23. N. Jiang, A.J. Ragauskas, Tetrahedron Lett. 48, 273 (2007)
- K.S. Coleman, M. Coppe, C. Thomas, J.A. Osborn, Tetrahedron Lett. 40, 3723 (1999)
- 25. J. Muldoon, S.N. Brown, Org. Lett. 4, 1043 (2002)
- 26. S.S. Kim, H.C. Jung, Synthesis, 14, 2135 (2003)
- 27. C.W. Jones, J.H. Clark, *Applications of hydrogen peroxide and derivatives* (Royal Society of Chemistry, UK, 1999)
- L. Marinescu, M. Molbach, C. Rousseau, M. Bols, J. Am. Chem. Soc. 127, 17578 (2005)
- 29. Y. Kon, Y. Usui, K. Sato, Chem. Commun. 14(42), 4399 (2007)
- A.A. Linden, M. Johansson, N. Hermanns, J.E. Backvall, J. Org. Chem. 71, 3849 (2006)
- 31. T. Hida, H. Nogusa, Tetrahedron 65, 270 (2009)
- 32. F. Shi, M.K. Tse, M. Beller, Adv. Synth. Catal. 349, 303 (2007)
- 33. F. van Rantwijk, R.A. Sheldon, Chem. Rev. 107, 2757 (2007)
- P. Wasserschein, T. Welton, *Ionic liquids in synthesis* (Wiley-VCH, Weinhein, 2003)
- M.A.P. Martins, C.P. Frizzo, D.N. Moreira, N. Zanatta, H.G. Bonacorso, Chem. Rev. 108, 2015 (2008)
- F.F. Yang, H.Y. Guo, Z.Y. Jiao, C.C. Li, J.Q. Ye, J. Iran. Chem. Soc. 9, 327 (2012)
- N.J. Roberts, G.J. Lye, Application of room temperature ionic liquids in biocatalysis: opportunities and challenges (American Chemical Society, Washington, DC, 2002)
- D.R. MacFarlane, M. Forsyth, P.C. Howlett, J.M. Pringle, J.Z. Sun, G. Annat, W. Neil, E.I. Izgorodina, Acc. Chem. Res. 40, 1165 (2007)
- 39. Y.J. Meng, V. Pino, J.L. Anderson, Anal. Chem. 81, 7107 (2009)
- 40. T. Ooi, K. Maruoka, Angew. Chem. Int. Ed. 46, 4222 (2007)
- 41. Z. Xi, N. Zhou, Y. Sun, K. Li, Science 292, 1139 (2001)
- 42. J.A. Gladysz, Chem. Rev. 102, 3215 (2002)
- S. Sunitha, S. Kanjilal, P.S. Reddy, B.N. Rachapudi, Tetrahedron Lett. 48, 6962 (2007)
- 44. A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis, J. Am. Chem. Soc. **124**, 5962 (2002)
- 45. B. Tan, J.Y. Jiang, Y.H. Wang, L. Wei, D.J. Chen, Z.L. Jin, Appl. Organomet. Chem. 22, 620 (2008)
- 46. Y. Leng, J. Wang, D.R. Zhu, X.Q. Ren, H.Q. Ge, L. Shen, Angew. Chem. Int. Ed. 48, 168 (2009)
- H.Z. Zhi, J. Luo, W. Ma, C.X. Lu, Chem. J. Chin. Univ. 29, 2007 (2008)

- 48. Y.L. Hu, X. Liu, T.T. Lu, M. Lu, Q. Ge, S.B. Zhang, J. Iran. Chem. Soc. 8, 131 (2011)
- 49. J. Porwoll, Aldrich advancing science: handbook of fine chemicals (Sigma-Aldrich Chemical Co., 2007–2008)
- 50. K. Surendra, K.N. Srilakshmi, R.M. Arjun, M. Nageswar, R.K. Rama, J. Org. Chem. 68, 2058 (2003)
- M. Zeng, Y. Du, L. Shao, C. Qi, X.M. Zhang, J. Org. Chem. 75, 2556 (2010)
- 52. C.J. Pouchart, The aldrich library of infrared spectra (Sigma-Aldrich Chemical Co., 1981)