



# Controlling the selectivity of the manganese/bicarbonate/hydrogen peroxide catalytic system by a biphasic pyrrolidinium ionic liquid/*n*-heptane medium



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## ABSTRACT

The  $\text{Mn}^{2+}/\text{HCO}_3^-/\text{H}_2\text{O}_2$  catalytic system exhibits excellent aldehyde selectivity in the oxidation of various benzylic and allylic alcohols under mild conditions and short reaction time when the reactions are carried out in a biphasic dicationic pyrrolidinium ionic liquid/*n*-heptane medium. The dicationic pyrrolidinium ionic liquid shows differential solubility towards alcohols and their aldehydes whereas the immiscible *n*-heptane instantaneously extracted and separated aldehydes from the reaction phase. This design of biphasic ionic liquid/*n*-heptane catalytic system prevents the over-oxidation of aldehydes to carboxylic acids effectively. Separation and recycling can also be easily done by decantation of the *n*-heptane layer after reaction. With the biphasic system, high conversion of benzyl alcohol to benzaldehyde was achieved with very low loadings of  $\text{H}_2\text{O}_2$  and  $\text{Mn}(\text{OAc})_2$  catalyst at room temperature and within short reaction time. Throughout 10 reaction cycles, a total turnover number (TON) of 37,600 was achieved and excellent catalytic reactivity and selectivity were maintained with an average yield of 94%.

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## 1. Introduction

Transition metal-catalyzed oxidation using bicarbonate-activated hydrogen peroxide as the terminal oxidant is considered a simple, effective and relatively environmentally benign catalytic system which can oxidize a variety of organic substrates including amino acids [1,2], alcohols and amines [3], sulfides [3–5], olefins [6–10], and organic dyes [11,12]. In these catalytic systems, the bicarbonate reacts with  $\text{H}_2\text{O}_2$  to give peroxydicarbonate ( $\text{HCO}_4^-$ ) [13], which is further activated by transition metal ions, in particular manganese, in the catalytic oxidation (Scheme 1). It has been proposed that a high valent manganese oxo species might be involved in the catalytic process [6]. However, the system exhibits only limited selectivity. In particular, primary alcohols are oxidized to a mixture of aldehydes and carboxylic acid [3], as further oxidation of the aldehydes produced to carboxylic acids occurs readily during the catalytic reactions.

Today, the development of oxidation systems that operate under mild reaction conditions with high product selectivity is still a challenging task [11–19]. To the best of our knowledge, the exploitation

of the  $\text{Mn}^{2+}/\text{HCO}_3^-/\text{H}_2\text{O}_2$  catalytic system for selective oxidation of alcohols to aldehydes has not been reported, although a number of Mn-catalyzed systems for alcohol oxidation are known [14–18]. We herein report our study on using a biphasic dicationic pyrrolidinium ionic liquid 1/*n*-heptane medium to provide differential solubility to the substrates and products in the  $\text{Mn}^{2+}/\text{HCO}_3^-/\text{H}_2\text{O}_2$  catalytic system which leads to excellent aldehyde selectivity in the catalytic oxidation of benzylic and allylic alcohols. *n*-Heptane was used as the extraction phase because it is an alternative greener solvent for the replacement of *n*-hexane and *n*-pentane in chemical processes [20]. The structures of the ionic liquids used in this study are shown in Scheme 2.

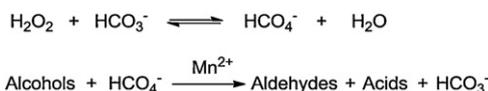
## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals were purchased from Aldrich or Acros Organic. All the solvents were of analytical reagent grade and were used without further purification. A Hewlett-Packard 8900 GC–MS equipped with EC-1 or EC-WAX columns (Alltech Associates, Inc.) was used for the determination of yield and the identification of reaction products.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 MHz NMR spectrometer. Tetradecane was used as an internal

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**Scheme 1.** Mechanism of bicarbonate-activated oxidation of alcohols.

standard in the quantitative GC–MS measurements. ESI-MS analysis was carried out by a Waters Acquity SQD Mass Spectrometer. Ionic liquids **2–4** were prepared according to literature reported procedures [21,22].

## 2.2. Preparation of di-cationic ionic liquid **1**

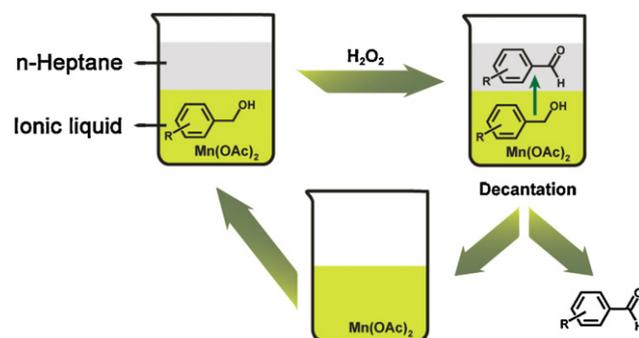
A solution of 1,6-dibromohexane (20 mL, 0.13 mol) was carefully added to 1-methylpyrrolidine (29 mL, 2.1 equiv.) in 100 mL acetonitrile. The mixture was gently heated to reflux under argon for 24 h. After cooling to room temperature, white solids of the bromide salt precipitated out. The solvent was decanted and the product was washed thoroughly with diethyl ether and dried under vacuum. The white solids (12.4 g, 0.03 mol) were further reacted with silver (I) oxide (16.7 g, 1.2 equiv.) in water to yield the ionic liquid with hydroxide as the counter anions. The silver bromide precipitates were removed by filtration and collected for recycling. After removal of solvent, the hydroxide product was obtained and re-dissolved in methanol. CO<sub>2</sub> gas was then purged directly for 30 min into the solution to afford the desired ionic liquid **1** with bicarbonate (HCO<sub>3</sub><sup>−</sup>) as the counter anions. An overall yield of 95% was obtained in the preparation. HR-MS: [**1**]<sup>2+</sup>: Found 127.1630, calc. 127.1361; [**1**]<sup>+</sup>: Found 315.2659, calc. 315.2648; <sup>1</sup>H NMR (D<sub>2</sub>O): δ 1.40–1.50 (m, 4H), 1.78–1.92 (m, 4H), 2.21 (s, 8H), 3.04 (s, 6H), 3.30–3.38 (m, 4H), 3.45–3.60 (m, 8H); <sup>13</sup>C NMR (D<sub>2</sub>O): δ 24.10, 25.80, 28.13, 50.85, 66.90, 67.10, 163.03.

## 2.3. General procedures for the oxidation of alcohols

To a 25 mL round-bottom flask, ionic liquid (5.6 mmol), Mn(OAc)<sub>2</sub> (0.025 mol%), alcohol (3 mmol), and *n*-heptane (6 mL) were added. De-ionized water (0.5 mL) was added to lower the viscosity of the mixture. The resulting solution was then kept stirring vigorously. Under ambient conditions, aqueous hydrogen peroxide (6 × 60 μL, 35 wt.% in water) was injected into the reaction mixture in 3 min intervals over 20 min. After the reaction had been completed, the *n*-heptane solution (upper layer) was carefully decanted from the ionic liquid medium. In order to completely extract the aldehyde from the ionic liquid with residual *n*-heptane, additional *n*-heptane (2 × 5 mL) was added and the combined organic solution was then dried over anhydrous sodium sulfate. After the removal of solvent under vacuum, the aldehyde was isolated as a colourless liquid and characterized by GC–MS and <sup>1</sup>H NMR. The *n*-heptane collected was reused in catalysis and extraction process. It was found that the use of *n*-heptane, *n*-hexane, *n*-pentane, or petroleum ether (40–60 °C) as the extraction phase in the catalysis showed no observable difference as these solvents are immiscible with the ionic liquid. However, heptane was chosen because it is considered as a greener alternative solvent for chemical processes [20].

## 2.4. Procedures for larger scale catalytic oxidation of benzyl alcohol

To a 500 mL round-bottom flask equipped with magnetic stirrer, **1** (70 g, 186 mmol) in de-ionized H<sub>2</sub>O (18 mL), Mn(OAc)<sub>2</sub> (0.025 mol%), benzyl alcohol (10.3 mL, 100 mmol), and *n*-heptane (200 mL) were added. The flask was placed in a water bath maintained at 20 °C. Aqueous hydrogen peroxide (12 mL, 35 wt.% in water) was then added dropwise to the reaction mixture over a



**Fig. 1.** A schematic diagram showing the use of biphasic ionic liquid/*n*-heptane in the selective oxidation of benzyl alcohol to benzaldehyde.

period of 40 min using a peristaltic pump. *Caution!* The reaction can be very exothermic if the hydrogen peroxide is added too quickly. Benzaldehyde was obtained as a colourless liquid in 83% yield by decantation of the *n*-heptane layer and additional extraction (*n*-heptane, 2 × 60 mL) from the ionic liquid medium. The crude product was characterized by GC–MS and <sup>1</sup>H NMR. The heptane was collected and recycled in the catalysis and extraction process.

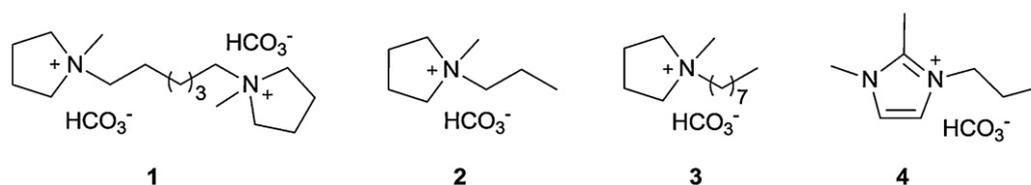
## 2.5. Procedures for recycling study

To a 25 mL round-bottom flask, **1** (5.6 mmol, 2.1 g), de-ionized H<sub>2</sub>O (500 μL), Mn(OAc)<sub>2</sub> (0.025 mol%), benzyl alcohol (310 μL, 3 mmol), and *n*-heptane (6 mL) were added. The mixture was then stirred vigorously. Aqueous hydrogen peroxide (6 × 60 μL, 35 wt.% in water) was injected into the reaction mixture over a period of 20 min. Benzaldehyde was obtained by decanting the *n*-heptane layer and further extraction from the ionic liquid with *n*-heptane (2 × 5 mL). The solution was dried over anhydrous sodium sulfate and *n*-heptane was removed under vacuum. The conversion of benzyl alcohol and the yield of benzaldehyde were determined with GC–MS. The recovered ionic liquid **1** was reused for the next cycle after removal of water by freeze-drying under vacuum.

## 3. Results and discussion

The cation of ionic liquid **1** consists of two *N*-methylpyrrolidinium groups, which are linked through a hexyl chain (Scheme 2). Bicarbonate was chosen to be the anion to provide a high concentration of HCO<sub>3</sub><sup>−</sup> in the medium so that the active peroxy-monocarbonate (HCO<sub>4</sub><sup>−</sup>) species can be generated effectively through the reaction with H<sub>2</sub>O<sub>2</sub> (Scheme 1). Ionic liquid **1** was synthesized by our previous reported procedures [23] with slight modifications and was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and high resolution MS. The highly polar nature of the **1** makes it immiscible with most non-polar organic solvents but allows certain miscibility with alcohols. We thus take advantage of this property to design a biphasic catalytic system in which the oxidation of alcohol occurs in the ionic liquid phase and the aldehyde produced is readily extracted into the upper *n*-heptane layer. A schematic diagram of the catalytic oxidation process is depicted in Fig. 1. The instantaneous separation of product from the reaction medium not only prevents the aldehyde from over-oxidation to carboxylic acid during the reaction, but also makes the separation simple and allows easy recovery of the ionic liquid and catalyst by decantation.

Benzyl alcohol was used as a model substrate to examine the catalytic ability and aldehyde selectivity of the biphasic system. After optimization of the catalytic system under various reaction conditions (Table 1 and Fig. 2), in a 3-mmol reaction where 0.025 mol % of Mn(OAc)<sub>2</sub> catalyst and 1.4 equiv. of H<sub>2</sub>O<sub>2</sub> were used, the conversion to benzaldehyde was almost completed (98 ± 1%) in 20 min at



**Scheme 2.** Ionic liquids for the biphasic catalytic systems.

**Table 1**  
Oxidation of benzyl alcohol to benzaldehyde by  $\text{Mn}(\text{OAc})_2\text{-H}_2\text{O}_2$  in ionic liquid/*n*-heptane at 25 °C for 20 min.<sup>a</sup>

Entry	$\text{Mn}(\text{OAc})_2$ (mol %)	Ionic liquid	$\text{H}_2\text{O}_2$ <sup>b</sup> (equiv.)	Conv. <sup>c</sup> (%)	Yield (%)	TON
1	0	<b>1</b>	1.4	0	–	–
2	0.0125	<b>1</b>	1.4	68	67 <sup>d</sup>	5360
3 <sup>f</sup>	0.025	<b>1</b>	1.4	98 ± 1	96 ± 1 <sup>e</sup>	3840
4	0.025	<b>1</b>	1.8	>99	70 <sup>d</sup>	2800
5	0.05	<b>1</b>	1.4	99	93 <sup>e</sup>	1860
6 <sup>f</sup>	0.025	<b>2</b>	1.4	91 ± 2	89 ± 3 <sup>d</sup>	3560
7	0.025	<b>3</b>	1.4	67	67 <sup>d</sup>	2680
8	0.025	<b>3</b>	2.8	96	40 <sup>d</sup>	3684
9	0.025	<b>4</b>	1.4	60	60 <sup>d</sup>	2400
10	0.025	<b>4</b>	2.8	77	32 <sup>d</sup>	2955

<sup>a</sup> Reaction conditions: benzyl alcohol 3 mmol, ionic liquid (5.6 mmol) in 0.5 mL water, 6 mL *n*-heptane, 1.4 equiv. of 35 wt.%  $\text{H}_2\text{O}_2$ .

<sup>b</sup> Number of equivalents with respect to benzyl alcohol.

<sup>c</sup> Conversion of benzyl alcohol determined by GC–MS.

<sup>d</sup> Yield estimated by GC–MS with tetradecane as the internal standard.

<sup>e</sup> Isolated yield.

<sup>f</sup> The reactions were repeated 5 times.

**Table 2**  
Catalytic oxidation of benzyl alcohol by  $\text{Mn}(\text{OAc})_2\text{-H}_2\text{O}_2$ /1 with acetonitrile as the reaction medium at 25 °C.<sup>a</sup>

Entry	$\text{H}_2\text{O}_2$ <sup>b</sup> (equiv.)	Temp. (°C)	Time (min)	Conv. (%) <sup>c</sup>	Benzaldehyde (%) <sup>f</sup>	Benzoic acid (%) <sup>f</sup>
1 <sup>d</sup>	1.4	25	20	0	0	0
2	1.4	25	20	48	46	2
3	2.8	25	40	84	80	4
4	4.2	25	60	90	85	5
5 <sup>e</sup>	4.2	50	40	91	60	31
6 <sup>f</sup>	1.4	25	20	88	14	74

<sup>a</sup> Reaction conditions: 6 mL  $\text{CH}_3\text{CN}$ , 3 mmol benzyl alcohol, 0.025 mol %  $\text{Mn}(\text{OAc})_2$ , 5.6 mmol (2.1 g) of **1** in 0.5 mL water, 35 wt.%  $\text{H}_2\text{O}_2$ .

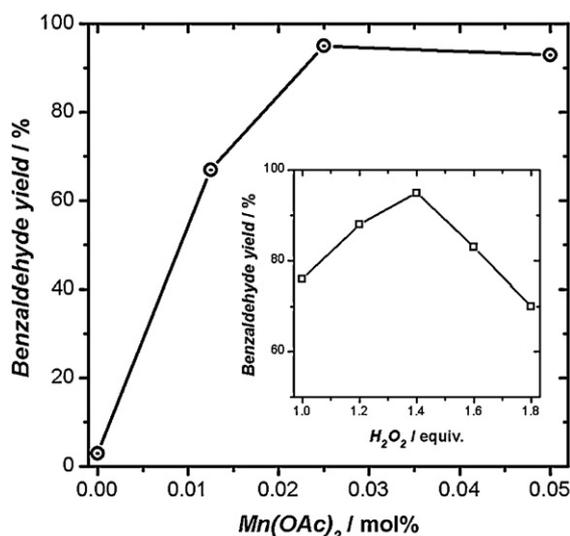
<sup>b</sup> Number of equivalents with respect to benzyl alcohol.

<sup>c</sup> The % yields were estimated by GC–MS.

<sup>d</sup> Without adding **1**.

<sup>e</sup> Reaction was carried out at 50 °C.

<sup>f</sup> Reaction was performed in ionic liquid medium only without any organic solvent.



**Fig. 2.** A study of the effect of  $\text{Mn}(\text{OAc})_2$  and  $\text{H}_2\text{O}_2$  (inset) loadings on the benzaldehyde selectivity.

room temperature with 96 ± 1% isolated yield and no benzoic acid was observed (Table 1, entry 3; TON = 3840). It is noteworthy that only 1.4 equiv. of  $\text{H}_2\text{O}_2$  were used in this system, which is a very low loading of oxidant for metal-catalyzed oxidation reactions. Further increase in the amount of  $\text{Mn}(\text{OAc})_2$  or  $\text{H}_2\text{O}_2$  resulted in reducing the selectivity of aldehyde due to over-oxidation [24]. As a comparison, when the monocationic ionic liquid **2**/*n*-heptane system was employed under the same conditions (Table 1, entry 6), the conversion of benzyl alcohol was not completed (91 ± 2%) and over-oxidation of benzaldehyde to benzoic acid was observed (1.5–5%). The aldehyde selectivity was found to be significantly less than that of **1**. The results probably reflect that **2** has better solubility for aldehydes and thus causes over-oxidation in the catalysis. Control experiments were performed under similar conditions but with **1** dissolved in acetonitrile in a single phase. Both benzaldehyde (46% yields) and benzoic acid (2% yields) were produced and 52% of benzyl alcohols remained un-oxidized in the reaction (Table 2, entry 2). This result is very poor in terms of reactivity and aldehyde selectivity compared to those obtained in the biphasic system shown in Table 1. Increasing the amount of  $\text{H}_2\text{O}_2$  in this single phase system did not enhance the conversion much but the amount of benzoic acid increased (Table 2, entries 3–4). When the reaction was carried

**Table 3**  
Solubility of benzaldehyde and benzyl alcohol in ionic liquid (1–4) solutions.<sup>a</sup>

Solubility (mmol/mL)	Ionic Liquid			
	1	2	3	4
Benzaldehyde	0.001	0.08	0.16	2.95
Benzyl alcohol	0.05	0.22	0.35	Miscible

<sup>a</sup> The solubility tests were carried out at room temperature and the ionic liquid solutions were prepared with 2.8 mmol ionic liquid + 0.25 mL H<sub>2</sub>O.

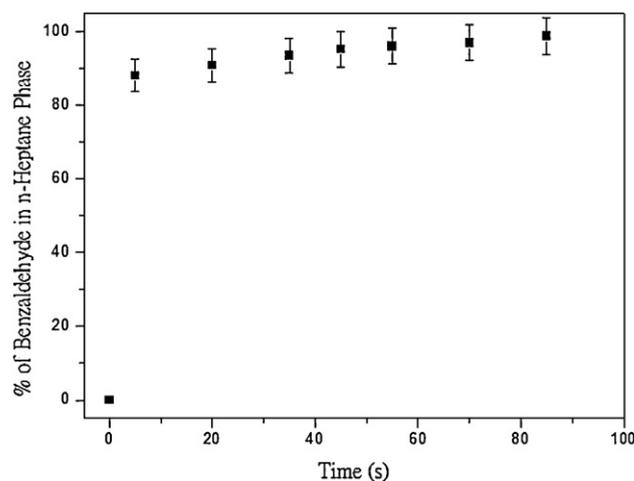
out in **1** only (no *n*-heptane), benzoic acid was produced as the major product (74% yields; Table 2, entry 6).

The amount of the ionic liquid **1** used in the biphasic catalytic oxidation reactions has an effect on the conversion. When 1.8 mmol (0.7 g) of **1** was used in the catalysis, the conversion of benzyl alcohol was only 72%. When the amount of the ionic liquid was increased to 3.6 mmol (1.4 g), the conversion was improved significantly to 91%. The conversion to benzaldehyde was almost completely (>99%) when 5.6 mmol (2.1 g) of **1** was used under the same conditions.

Other more hydrophobic and less polar ionic liquids (**3** and **4** in Scheme 2) were also examined under the same reaction conditions in order to compare their reactivity and aldehyde selectivity in the biphasic catalytic system (Table 1, entries 7–10). It was found that both **3** and **4** formed emulsion with *n*-heptane upon vigorous stirring. In a 20-min catalytic reaction, the conversion of benzyl alcohol was only 67% and 60% for **3** and **4** respectively which are significantly lower than that of **1**. The low conversion may be attributed to the formation of emulsion of the ionic liquid with *n*-heptane that retarded the action of the catalyst. The formation of emulsion also made the subsequent separation more difficult. When the reaction time was extended to 40 min with the amount of H<sub>2</sub>O<sub>2</sub> increased to 2.8 equiv., 96% conversion of benzyl alcohol was achieved for ionic liquid **3** but serious over-oxidation to benzoic acid was observed (yield of benzaldehyde 40%, benzoic acid 56%; Table 1, entry 8). For ionic liquid **4**, the conversion improved from 60% to 77% when reaction was performed with 2.8 equiv. of H<sub>2</sub>O<sub>2</sub> for 40 min. However, the yield of benzaldehyde was only 32% whereas that of benzoic acid was 45% (Table 1, entries 9 and 10).

As the differential solubility of aldehydes in the ionic liquid and *n*-heptane phases is crucial for selective oxidation, the solubility of benzaldehyde and benzyl alcohol in ionic liquids **1–4** was investigated. The experiments were performed at room temperature in the ionic liquids under conditions similar to those used for the catalytic reaction. The results are summarized in Table 3. It was found that benzaldehyde exhibited very low solubility (about 0.001 mmol/mL) in ionic liquid **1** under the reaction condition while the solubility in ionic liquid **2** is 0.08 mmol/mL. The solubility of benzaldehyde increased significantly in ionic liquids **3** and **4**. Among these ionic liquids, **4** has the highest solubility for benzaldehyde (2.95 mmol/mL). For the solubility of benzyl alcohol, a similar trend related to the polarity and hydrophobicity of the ionic liquids was observed. The most polar di-cationic ionic liquid **1** exhibited the lowest solubility for benzyl alcohol (0.05 mmol/mL), whereas ionic liquid **4** was found to be completely miscible with benzyl alcohol.

As indicated from the solubility test results, benzaldehyde shows very low solubility in ionic liquid **1** (Table 3). This implies that the benzaldehyde produced could be extracted to the *n*-heptane phase effectively from the ionic liquid reaction phase during the catalysis. A kinetic study on the transfer of benzaldehyde in the biphasic ionic liquid **1**/*n*-heptane system was performed and the results are depicted in Fig. 3. It was found that about 90% of the benzaldehyde in the ionic liquid phase was transferred to the *n*-heptane phase during the first 5 s of the experiment. The amount of benzaldehyde in the *n*-heptane phase kept increasing and reached 99% within 90 s. These results confirmed that the aldehyde produced in **1** could be rapidly transferred into the *n*-heptane

**Fig. 3.** Transfer kinetics of benzaldehyde in the biphasic ionic liquid **1**/*n*-heptane system.

layer during the oxidation reaction and over-oxidation was thus prevented.

The recyclability of the Mn-catalyzed biphasic system was also investigated. Throughout 10 reaction cycles (Table 4), excellent catalytic reactivity and selectivity were maintained and an average yield of 94% was obtained. A high turnover number (total TON = 37,600 in 10 reaction cycles) obtained in the recycling study demonstrates the robustness and stable performance of the ionic liquid system for oxidation reactions. For a larger scale reaction with 100 mmol benzyl alcohol, the reaction proceeded smoothly and 97% conversion of benzyl alcohol was achieved in 40 min (Table 5, entry 3). In addition, some substituted benzylic alcohols (Table 5, entries 4–6) also give good selectivity and yields to the corresponding aldehydes.

In the recycling study, water from the aqueous H<sub>2</sub>O<sub>2</sub> accumulated in the ionic liquid layer and was removed by freeze-drying to maintain the catalytic efficiency. The necessity to remove water from the reaction medium reduced the simplicity of the catalytic system. The effect of the accumulated water in the ionic liquid was thus investigated. After each reaction, the *n*-heptane layer was separated and the ionic liquid medium was rinsed three times with *n*-heptane. The ionic liquid medium together with the accumulated water was then reused for the next experiment. *n*-Heptane, benzyl alcohol and H<sub>2</sub>O<sub>2</sub> solution (410 μL, dropwise) were freshly added for the catalytic reaction. The recycling results are listed in Table 6. In the first two cycles, the good performance of the catalytic system was maintained (98–99% conversion). However, the conversion of benzyl alcohol was found to decrease to 91% on its third run. As more water was accumulated (1.7–2.1 mL approximately) in the ionic liquid phase, the conversion of benzyl alcohol further declined (Table 6, run 4: 68%, no benzoic acid was produced) which can be attributed to the dilution effect caused by the accumulated water. These results also indicate that the removal of water from the ionic liquid medium is necessary at the third cycle in order to maintain the good performance of the biphasic catalytic system.

**Table 4**  
Recycling results in the oxidation of benzyl alcohol to benzaldehyde.<sup>a</sup>

No. of cycle	1	2	3	4	5	6	7	8	9	10
Conversion (%)	99	98	96	97	99	99	98	99	97	98
Yield (%)	96	94	92	93	96	93	94	96	94	93

<sup>a</sup> Conversion and yield were estimated by GC–MS based on 3 mmol of benzyl alcohol. The water content in the ionic liquid medium was removed by freeze-drying under vacuum after each cycle.

**Table 5**  
Selective oxidation of benzylic and allylic alcohols in **1**/*n*-heptane biphasic system with Mn(OAc)<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>.<sup>a</sup>

Entry	Alcohols	H <sub>2</sub> O <sub>2</sub> <sup>b</sup> (equiv.)	Time (min)	Yield (%)	Conv. (%) <sup>d</sup>	TON <sup>e</sup>
1	Benzyl alcohol	1.4	20	95 <sup>c</sup>	99	3800
2 <sup>f</sup>	Benzyl alcohol	1.4	20	94 <sup>i</sup>	98	37600 <sup>g</sup>
3 <sup>h</sup>	Benzyl alcohol	1.4	40	83 <sup>c</sup>	97	3320
4	4-Methoxybenzyl alcohol	1.4	20	97 <sup>j</sup>	99	3880
5	4-Methylbenzyl alcohol	1.9	30	95 <sup>j</sup>	99	3800
6	4-Fluorobenzyl alcohol	1.4	20	95 <sup>j</sup>	99	3800
7	<i>trans</i> -Cinnamyl alcohol	1.4	20	96 <sup>j</sup>	99	3840
8 <sup>i</sup>	<i>trans</i> -Cinnamyl alcohol	1.4	20	70 <sup>j</sup>	99	2800
9	3-Methyl-2-buten-1-ol	1.4	20	85 <sup>j</sup>	86	3400
10	2-Buten-1-ol	1.4	20	7 <sup>j</sup>	77	280
11	1-Phenylethanol	1.4	30	71 <sup>k</sup>	73	2840
12 <sup>l</sup>	1-Phenylethanol	4.2	40	98 <sup>k</sup>	99	3920

<sup>a</sup> Reaction conditions: 3 mmol alcohol, 0.025 mol % Mn(OAc)<sub>2</sub>, 5.6 mmol (2.1 g) of **1** in 0.5 mL water, 6 mL *n*-heptane, 25 °C.

<sup>b</sup> Number of equivalents of H<sub>2</sub>O<sub>2</sub> (35 wt.%) with respect to alcohol.

<sup>c</sup> Isolated yield of aldehyde.

<sup>d</sup> Conversion of alcohols.

<sup>e</sup> TON are calculated based on yields of aldehyde.

<sup>f</sup> Recycling for 10 reaction cycles.

<sup>g</sup> Total turnover number in 10 reaction cycles.

<sup>h</sup> Reaction scale in 100 mmol alcohol.

<sup>i</sup> Reaction was performed in **1** without *n*-heptane; *trans*-cinnamic acid produced in 30% yield.

<sup>j</sup> Yield was determined by GC-MS.

<sup>k</sup> Yield of acetophenone determined by GC-MS.

<sup>l</sup> Reaction was taken place at 45 °C.

**Table 6**  
The effect of accumulated water content in the catalytic reaction.<sup>a</sup>

Run	H <sub>2</sub> O content (mL)	Conversion (%)
1	0.9	99
2	1.3	98
3	1.7	91
4	2.1	68

<sup>a</sup> Reaction conditions: Benzyl alcohol 3 mmol, ionic liquid **1** 5.6 mmol (2.1 g) in 0.5 mL water, 6 mL *n*-heptane, 1.4 equiv. of 35 wt.% H<sub>2</sub>O<sub>2</sub> (410 μL) at 25 °C; water was not removed for the next run; yields were estimated by GC-MS based on 3 mmol of benzyl alcohol.

As indicated from all the experimental results, the Mn-catalyzed biphasic system is highly selective and efficient in the transformation of alcohols to aldehydes under mild conditions. We believe that the excellent selectivity can be attributed to the highly polar nature of **1** which controls the solubility of substrates (benzylic alcohols, soluble in ionic liquid layer) and the oxidized products (aldehydes, less soluble in ionic liquid layer) during the reaction. As a result, the benzylic alcohols were effectively oxidized in the ionic liquid phase. At the same time, the produced aldehydes, which are more soluble in *n*-heptane, were immediately extracted into the upper *n*-heptane phase and therefore protected from over-oxidation.

The Mn-catalyzed biphasic system also works well for some allylic alcohols with excellent functional group selectivity (Table 5, entries 7–10). *trans*-Cinnamyl alcohol was selectively oxidized to *trans*-cinnamaldehyde with good yields (96%) and the internal

**Table 7**  
The electronic effect of substrates in the catalytic system of Mn(OAc)<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> in **1**/*n*-heptane at 25 °C.<sup>a</sup>

Entry	Alcohols	H <sub>2</sub> O <sub>2</sub> <sup>b</sup> (equiv.)	Time (min)	Conv. <sup>c</sup> (%)	Yield <sup>d</sup> (%)
1	4-Methoxybenzyl alcohol	1.4	20	99	97
2	3,4-Dimethoxy-benzyl alcohol	1.4	30	93	89 <sup>e</sup>
3	4-Methylbenzyl alcohol	1.9	30	99	95
4	4-Fluorobenzyl alcohol	1.4	20	99	95
5	4-Chlorobenzyl alcohol	2.4	60	99	93 <sup>e</sup>
6	4-Trifluoromethyl benzyl alcohol	2.4	60	87	85 <sup>e</sup>
7	4-Nitrobenzyl alcohol	2.4	60	40	38 <sup>e</sup>

<sup>a</sup> Reaction conditions: 3 mmol alcohol, 0.025 mol % Mn(OAc)<sub>2</sub>, ionic liquid medium: 5.6 mmol (2.1 g) of **1** in 0.5 mL water, 1.4–2.4 equiv. of 35 wt.% H<sub>2</sub>O<sub>2</sub>, 6 mL *n*-heptane.

<sup>b</sup> Number of equivalents with respect to benzyl alcohol.

<sup>c</sup> Conversion of alcohol determined by GC-MS.

<sup>d</sup> Yield estimated by GC-MS with tetradecane as an internal standard.

<sup>e</sup> Isolated yield of aldehyde.

C=C bond remained intact. When the oxidation of *trans*-cinnamyl alcohol was performed in the ionic liquid medium without *n*-heptane, the internal C=C bond was not oxidized but a significant amount of *trans*-cinnamic acid was produced (30%, Table 5, entry 8). However, when increasing the amount of H<sub>2</sub>O<sub>2</sub> (2.8 equiv.) with longer reaction time, a small amount of 3-phenyloxirane-2-carbaldehyde (6%) was obtained, and the yield of *trans*-cinnamaldehyde was significantly reduced to 51% due to over-oxidation to *trans*-cinnamic acid (42%). For 2-buten-1-ol, serious over-oxidation to the corresponding carboxylic acid (yield = 70%; Table 5, entry 10) was observed. However, the C=C bond was found to remain intact in the reaction. The secondary alcohol 1-phenylethanol was also examined and it was found to be less reactive than the benzylic/allylic alcohols. For a reaction with 4.2 equiv. of H<sub>2</sub>O<sub>2</sub> at 45 °C for 40 min, an excellent yield of acetophenone (98%) was obtained (Table 5, entries 11 and 12).

The electronic effect of substrates on the reaction was also explored using different benzyl alcohols and the results are summarized in Table 7. In general, the system shows better reactivity towards the electron-rich benzyl alcohols. The *p*-substituted benzyl alcohols (MeO, Me, Cl, and F) gave comparable results in both conversion (93–99%) and aldehyde selectivity (94–98%), but the electronic effect of the chloro-substituent was manifested by the longer reaction time and larger amount of H<sub>2</sub>O<sub>2</sub> needed in the oxidation of 4-chlorobenzyl alcohol (2.4 equiv. H<sub>2</sub>O<sub>2</sub> for 60 min). For the electron-deficient 4-trifluoromethyl benzyl alcohol, it also took a longer reaction time (60 min) and more H<sub>2</sub>O<sub>2</sub> (2.4 equiv.) in

the catalysis. A lower conversion of 87% was obtained in the reaction. In the case of 4-nitrobenzyl alcohol, only 40% conversion was observed under the same reaction conditions.

#### 4. Conclusions

In summary, a new biphasic catalytic system using  $\text{Mn}(\text{OAc})_2$  and  $\text{H}_2\text{O}_2$  in a dicationic pyrrolidinium-based bicarbonate ionic liquid with an immiscible *n*-heptane layer has been developed for rapid and selective oxidation of benzylic and allylic alcohols to aldehydes under mild reaction conditions. The high selectivity for aldehyde production in the system benefits from the dicationic ionic liquid which allows good solubility for alcohols but is immiscible with *n*-heptane. In addition, the system shows good selectivity for the internal C=C bond versus the terminal hydroxyl group in the oxidation reaction. The system also demonstrates excellent performance in a 100-mmol reaction scale with only 1.4 equiv. of  $\text{H}_2\text{O}_2$  and maintains its high reactivity and selectivity upon recycling for 10 times. A very high turnover number up to 37,600 was achieved in the recycling study for 10 reaction cycles. The ease of separation of products makes this protocol a very convenient process.

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- [24] Aldehyde selectivity was found more sensitive to the amount of  $\text{H}_2\text{O}_2$  used (see Fig. 2), and slow addition of  $\text{H}_2\text{O}_2$  is necessary to obtain good alcohol conversion and high benzaldehyde selectivity.