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# Confining task-specific ionic liquid in silica-gel matrix by sol-gel technique: A highly efficient catalyst for oxidation of alcohol with molecular oxygen

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# **1. Introduction**

In the past decade, ionic liquids (ILs) have attracted increasing attention in organic synthesis and catalysis. The favorable characteristics, such as low vapor pressure, high thermal stability, and peculiar ion environment, make ILs "green" alternatives for replacing traditional organic solvents. As both the anionic and the cationic part of ILs can be easily varied, the physical and chemical properties of ILs can be finely tuned. So ILs can be used as good solvents for a broad spectrum of inorganic, organic and polymeric materials. However, ionic liquids are still expensive even though being commercially available. Furthermore, the high viscosity of ILs may induce mass transfer limitations if the chemical reaction is fast, causing the reaction to proceed in the diffusion layer of the catalyst, rather than in the bulk solvent. Thus from economic and environmental viewpoint, homogeneous catalysis in ILs is unattractive.

One solution to improve catalysis with ILs is the immobilization of ionic liquid phase containing the transition metal catalysts on the surface or pores of various porous solid materials via covalent bonding, adsorption or sol-gel process[1]. Compared with pure ionic liquids, these immobilized ionic liquids show additional advantages, such as significantly decrease of the amounts of ionic liquid, the

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#### ABSTRACT

A novel catalytic system was developed through confinement of TEMPO task-specific ionic liquid (TEMPO-IL) with CuCl<sub>2</sub> in a silica-gel matrix by sol-gel technique. The obtained TEMPO-IL/CuCl<sub>2</sub>/silica-gel catalytic system was effective for the transformation of a series of benzylic, allylic and heterocyclic alcohols to the respective carbonyl compounds under O<sub>2</sub> atmosphere. Notably, the system facilitates ease separation of the catalyst and product and shows good reusability in the reaction.

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facilitation of catalyst separation from reaction system and more rapid mass transfer, lower contamination of product, and the ability of using it in gas phase reactions[2]. However, chemical bonding of ILs fragments (anion or cation) onto a solid surface may limit the degrees of freedom of the counterparts and even change the physicochemical properties of ILs. As for physical adsorption, the main drawback is the risk of leaching of ILs and transition metal catalysts under rigorous reaction conditions.

Different from the former methods, the immobilization of ILs by sol-gel process results in a more intimate biphasic system. The solid matrix forms a porous prison that prevents ILs or transition metal catalysts from leaching, but allows the free transportation of reactants and products[3]. Recently, supported ionic liquid catalysts by sol-gel method have been examined for carbonylation [4], hydroformylation [5], and alcohol oxidation [6]. In these reactions, catalytic activities were remarkably enhanced with decreased consumption of ILs compared to bulk ionic-liquid catalyst system.

The selective oxidation of alcohols to the corresponding aldehydes or ketones is the foundation of many important industrial and finechemical processes[7]. Many highly efficient aerobic alcohol oxidation systems either catalyzed by transition metal catalysts alone (such as palladium[8], gold[9–13], ruthenium[14,15], copper[16,17], iron [18,19], and vanadium[20]) or in combination with nitroxyl radical 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) have been developed.

Our recent work was focused on the oxidation of organic compounds with molecular oxygen as oxidant[21,22]. Earlier, we disclosed a catalytic system of TEMPO-IL/CuCl/MS3A (molecular sieve 3A) for the aerobic oxidation of a wide range of benzylic alcohols in ionic liquids

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[bmim]PF<sub>6</sub>, where MS3A serves as a heterogeneous Brønsted base to enhance the reaction rate remarkably[23]. In light of the newly developed supported ionic liquid catalyst systems, in this work, an attempt has been made to entrap task-specific ionic liquid immobilized TEMPO (TEMPO-IL) and transition metal salt into the pores of solid silica-gel by sol-gel method (Scheme 1). After great effort, a silica-gel supported task-specific ionic liquid catalyst system (TEMPO-IL/CuCl<sub>2</sub>/ silica-gel )was successfully prepared and shown to be effective for the transformations of a wide range of alcohols, including benzylic, allylic and heterocyclic alcohols, under mild conditions to the corresponding aldehydes in high conversions and selectivities. The TEMPO-IL/CuCl<sub>2</sub>/ silica-gel catalyst can easily be separated from the oxidation system and reused, which makes the system eco-friendly and cost-effective.

### 2. Experimental

#### 2.1. General

All chemicals were obtained from commercial resources with more than 99% purity and used without prior purification. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 equipped with a 30 m×0.32 mm×0.5  $\mu$ m HP-Innowax capillary column and a flame ionization detector. The elemental analysis of copper was determined by ICP-AES (Thermo icap6300). Products were all known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

# 2.2. Catalyst preparation

The ionic liquid [bmim]PF<sub>6</sub> was synthesized according to literature [24]. TEMPO-IL was prepared according to literature[25]. Typically, to a stirred solution of TEMPO-IL (0.5 g, 1.13 mmol) and [bmim]PF<sub>6</sub> (3.5 g) in 8 mL of methanol,  $CuCl_2 \cdot 2H_2O$  (0.193 g, 1.13 mmol) and water (0.5 mL) were added. The solution was then heated to 60 °C, and tetraethoxyorthosilicate (TEOS, 11 mL) was added. After the formation of a clear and homogeneous liquid mixture, hydrochloric acid (2 mol/L, 1 mL) was added dropwise and the mixture gradually coagulated. After aging at 60 °C for 24 h, the resultant solid material was dried in vacuum at 80 °C overnight and 6.3 g of catalyst (TEMPO-IL/CuCl<sub>2</sub>/silica-gel) was obtained (Fig. 1).

## 2.3. Typical experimental procedure for oxidation of alcohols

Alcohol (0.5 mmol) and catalyst (100 mg) were mixed with *n*-octane (5 mL) and stirred at 50 °C under O<sub>2</sub> (10 mL/min, 1 atm.) for given time. After completion (monitored by TLC and GC), the mixture was centrifuged to separate the catalyst, which was washed several times with *n*-octane, dried and recharged with fresh substrate and solvent for the next catalytic cycle. The combined solvent phase was concentrated under vacuum, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to provide the analytically pure aldehyde which was characterized by <sup>1</sup>HNMR and IR analysis.



Scheme 1. Aerobic oxidation of alcohols catalyzed by TEMPO-IL/CuCl<sub>2</sub>/silica-gel.



Fig. 1. Illustration of the synthesis of silica-gel-confined TEMPO-IL with CuCl<sub>2</sub>.

### 3. Results and discussion

#### 3.1. Effects of catalysts on the oxidation of alcohol

The catalysts prepared with different transition-metal salts and various amount of ionic liquid [bmim]PF<sub>6</sub> and hydrochloric acid were applied to the *p*-methoxybenzyl alcohol oxidation. The results were listed in Table 1. First, the amount of [bmim]PF<sub>6</sub> used in the preparation of catalyst has an important effect on the catalytic activity (entries 1–3). Only 18% of conversion was achieved in 3 h when the catalyst without additional ionic liquid was used. The presence of additional ionic liquid resulted in the increase of conversion. With the addition of 3.5 g [bmim] PF<sub>6</sub> in the preparation of catalyst, benzyl alcohol was completely oxidized into benzaldehyde within 3 h. Next, increasing the amount of acid used in the synthesis process of catalyst from 1 mL to 4 mL resulted in decrease of the conversion of the alcohol and selectivity to aldehyde (entries 3, 4). Lower conversion and selectivity may be ascribed to the side reaction caused by the existence of excess acid. Finally, a series of inexpensive transition-metal salts including CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Cu(OAc)<sub>2</sub>, FeCl<sub>3</sub>, NiCl<sub>2</sub>, Mn(OAc)<sub>2</sub> and Co(OAc)<sub>2</sub> were tested as co-catalyst with TEMPO-IL to oxidize *p*-methoxybenzyl alcohol to aldehyde. It can be seen that among the salts tested, copper salts showed much higher

 Table 1

 Effects of catalysts on the oxidation of *p*-methoxybenzyl alcohol.<sup>a</sup>

Entry	Catalyst	[bmim] PF <sub>6</sub> /g	Acid/ mL	Time/ h	Conv./ %	Select./ %
1	TEMPO-IL/CuCl <sub>2</sub> /silica-gel	-	1	3	18	>99
2	TEMPO-IL/CuCl <sub>2</sub> /silica-gel	1.5	1	3	84	>99
3	TEMPO-IL/CuCl <sub>2</sub> /silica-gel	3.5	1	3	100	>99
4	TEMPO-IL/CuCl <sub>2</sub> /silica-gel	3.5	4	3	81	85
5	TEMPO-IL/Cu(NO <sub>3</sub> ) <sub>2</sub> /silica-gel	3.5	1	3	95	>99
6	TEMPO-IL/Cu(OAc) <sub>2</sub> /silica-gel	3.5	1	3	90	>99
7	TEMPO-IL/FeCl <sub>3</sub> /silica-gel	3.5	1	12	63	72
8	TEMPO-IL/NiCl <sub>2</sub> /silica-gel	3.5	1	12	42	89
9	TEMPO-IL/Mn(OAc) <sub>2</sub> /silica-gel	3.5	1	12	51	83
10	TEMPO-IL/Co(OAc) <sub>2</sub> /silica-gel	3.5	1	12	55	85
11 <sup>b</sup>	TEMPO-IL/CuCl <sub>2</sub>	-	-	3	58	>99
12 <sup>c</sup>	acetamido-TEMPO/CuCl <sub>2</sub> /DMAP	-	-	5	52	>99

<sup>a</sup> Catalyst preparation: TEMPO-IL (0.5 g, 1.13 mmol), [bmim]PF<sub>6</sub>, metal salts (1.13 mmol), TEOS (11 mL), hydrochloric acid (2 mol/L), water (0.5 mL) and methanol (8 mL); oxidation reaction conditions: *p*-methoxybenzyl alcohol (0.5 mmol), catalyst (100 mg) and *n*-octane (5 mL) under  $O_2$  at 50 °C.

 $^{\rm b}$  p-methoxybenzyl alcohol (0.5 mmol), TEMPO-IL (0.0175 mmol) and  ${\rm CuCl_2}$  (0.0175 mmol).

 $^{\rm c}$  Reference [26], in [bmim]PF<sub>6</sub>, 5 mol% acetamido-TEMPO, 5 mol% CuCl<sub>2</sub>, 10 mol% DMAP under O<sub>2</sub> at r.t.



Fig. 2. Effects of solvents on the oxidation of alcohol. Reaction conditions: *p*-methoxybenzyl alcohol (0.5 mmol), TEMPO-IL/CuCl<sub>2</sub>/silica-gel (100 mg), and solvent (5 mL), under  $O_2$  at 50 °C, 3 h.

catalytic activity than other transition metal salts. All three copper salts ( $Cl^-$ ,  $NO_3^-$  and  $OAc^-$  salts) gave similar catalytic activity and identical selectivity (entries 3, 5, 6). In the case of Fe, Ni, Mn and Co salts,

Table 2Catalytic aerobic oxidation of various alcohols.<sup>a</sup>



**Fig. 3.** Recycling of the catalytic system for the oxidation of *p*-methoxybenzyl alcohol. Reaction conditions: *p*-methoxybenzyl alcohol (0.5 mmol), TEMPO-IL/CuCl<sub>2</sub>/silica-gel (100 mg), and *n*-octane (5 mL), under O<sub>2</sub> at 50 °C.

the oxidation of *p*-methoxybenzyl alcohol was relatively slow with only 42–63% conversion even after 12 h and the formation of carboxylic acid and its esters was observed (entries 7–10). Compared with acetamido-

Entry	Substrate	Product	Time/h	Conv./Select. <sup>b</sup> %	Yield <sup>c</sup> /%
1	ОН		3	100/>99	92
2	O <sub>2</sub> N OH	0 <sub>2</sub> N 0	4.5	100/>99	92
3	СІ		4	100/>99	91
4	Н3СО ОН	H <sub>3</sub> CO	3	100/>99	93
5 <sup>d</sup>	Н3СО ОН	H <sub>3</sub> CO	8	97/>99	92
6 <sup>e</sup>	Н3СО ОН	H <sub>3</sub> CO	2.5	100/>99	93
7	Н3С ОН	H <sub>3</sub> C	3.5	100/>99	92
8	CH <sub>3</sub> OH	CH <sub>3</sub>	4	100/>99	91
9	OH OH		8	99/>99	90
10	ОН		5.5	96/>99	84
11	ОН		3.5	97/97	85
12	n-C <sub>11</sub> H <sub>23</sub> -CH <sub>2</sub> OH	n-C <sub>11</sub> H <sub>23</sub> -CHO	15	35/>99	-

<sup>a</sup> Reaction conditions: alcohol (0.5 mmol), TEMPO-IL/CuCl<sub>2</sub>/silica-gel (100 mg), and *n*-octane (5 mL) under O<sub>2</sub> at 50 °C.

<sup>b</sup> GC conversion and selectivity.

<sup>c</sup> Isolated yield.

<sup>d</sup> Reaction temperature was 30 °C.

<sup>e</sup> Reaction temperature was 85 °C.

TEMPO/CuCl<sub>2</sub>/DMAP homogeneous system (entry 12), the present TEMPO-IL/CuCl<sub>2</sub>/silica-gel system showed favorable activity.

#### 3.2. Effects of solvents on the oxidation of alcohol

The solvents employed were crucial for the successful oxidation of *p*methoxybenzyl alcohol (Fig. 2). In *n*-octane, *p*-methoxybenzyl alcohol was completely oxidized into corresponding aldehyde within 3 h. High catalytic activities in the *n*-octane may be attributed to the stability of the catalytic system in the solvent and high-concentration of ionic liquids in the pores of silica matrix [4]. In solvents such as toluene and [bmim]PF<sub>6</sub>, the rate of oxidation was significantly slower. In DMF, the reaction almost stopped. The decrease in catalytic activity in these solvents may be due to the dissolution of TEMPO-IL. In these cases, the reaction was not limited in the pores of silica matrix but extend to the whole solvent. Consequently, they are actually homogeneous catalyst systems, intrinsically different from those in *n*-octane. Other factors such as the solubility of O<sub>2</sub> in solvent, the polarity and viscosity of solvent may have influence on the reaction, too.

# 3.3. Aerobic oxidation of alcohols promoted by TEMPO-IL/CuCl<sub>2</sub>/silica-gel

Based on the results above, we studied oxidation of different alcohols catalyzed by TEMPO-IL/CuCl<sub>2</sub>/silica-gel in *n*-octane and the results were listed in Table 2. All benzylic alcohols can be converted into corresponding aldehydes in high conversions within 8 h (entries 1-9). Similar reactivity was observed in the oxidation of substrates with electron-withdrawing or donating groups in the aromatic ring. Benzyl alcohols with methyl substitution on the o- or p- position all served as good substrates, which indicated that the steric effect of the substitution did not apparently affect the efficiency of the oxidation. To further probe the potential of the new catalyst system, we carried out the reaction at 30 °C. With prolonging the reaction time to 8 h, 97% of p-methoxybenzyl alcohol was transformed into aldehyde, demonstrate that the catalytic system of TEMPO-IL/CuCl<sub>2</sub>/silica-gel was highly effective. When the temperature was increased to 85 °C, a full conversion was obtained within only 2.5 h. Moreover, allylic and heterocyclic primary alcohols were also very smoothly oxidized to the corresponding aldehydes with high conversions and selectivities (entries 10 and 11). Double bond was unaffected. Compared to benzylic, allylic and heterocyclic alcohols, aliphatic alcohol was rather difficult to oxidize under the same conditions and the conversion was quite low even after 15 h (entry 12).

#### 3.4. Recycling of the catalytic system

The recyclability of the catalyst system was examined for the aerobic oxidation of *p*-methoxybenzyl alcohol in *n*-octane (Fig. 3). After reuse of the TEMPO-IL/CuCl<sub>2</sub>/silica-gel catalyst for five times, the conversion of the reactant decreased gradually from 100% to 87%, while the selectivity to aldehyde kept unchanged. To investigate the stability of different species confined in silica-gel, a series of analysis on the supernatant fraction were carried out after the reaction. In the supernatant fraction, Cu was not detected by ICP analysis, whereas trace TEMPO-IL species was detected by HPLC analysis. There is no

bonding between TEMPO-IL and silica gel. The leaching of TEMPO-IL under drastic reaction conditions is inevitable, which might be the main reason for the loss of activity.

#### 4. Conclusions

In conclusion, we have successfully developed a novel catalytic system by the confinement of task-specific ionic liquid (TEMPO-IL) and transition metal salt within a silica-gel matrix through sol-gel method. It was found that TEMPO-IL/CuCl<sub>2</sub>/silica-gel catalyst system was highly efficient for the aerobic oxidation of various alcohols. In addition, the catalyst does not lose catalytic activity and selectivity for at least five runs.

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