



Editor Choice paper

Molecular sieve promoted copper catalyzed aerobic oxidation of alcohols to corresponding aldehydes or ketones

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ABSTRACT

A novel combination of catalyst system of CuCl/TEMPO-IL/MS3A, which catalyzed the aerobic oxidation of alcohols in ionic liquid [bmim][PF₆] into aldehydes or ketones in high yields and selectivity, was reported. Molecular sieve 3A was found to have a significant beneficial effect on the catalytic reactions. The beneficial effect of Molecular sieve 3A was attributed to its Brønsted base property. With TEMPO being immobilized on ionic liquid to form TEMPO-IL and the use of a heterogeneous promoter of MS3A, the catalyst system could easily be recycled and reused without loss in catalytic activity.

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1. Introduction

The selective oxidation of alcohols to the corresponding aldehydes or ketones is a fundamental transformation both in laboratory synthesis and industrial production [1]. Numerous oxidizing reagents [2] (for example, CrO₃, KMnO₄, MnO₂, etc.) in stoichiometric amount have been traditionally employed to accomplish this transformation with considerable drawbacks such as the use of expensive reagents and volatile organic solvents, and discharge of environmentally pernicious wastes. From economic and environmental perspectives, the use of molecular oxygen as terminal oxidant has received great attention. Many highly efficient systems have been developed for catalytic aerobic alcohol oxidation using transition metals alone (such as palladium [3–5], ruthenium [6,7], copper [8–12], cobalt [13], vanadium [14]) or in combination with the nitroxyl radical 2,2,6,6-tetramethyl-piperidyl-1-oxyl (TEMPO) [15]. Of particular interest are the catalytic systems consisting of an inexpensive transition metal compound and TEMPO for mild and selective aerobic alcohol oxidations.

Since the first practical example of the Cu-catalyzed oxidation of alcohols using molecular oxygen as a stoichiometric oxidant in 1984 [16], many efforts have been made to find a synthetically useful method for Cu-catalyzed oxidation. Ansari and Gree reported a CuCl/TEMPO catalytic system, which aerobically oxidizes both

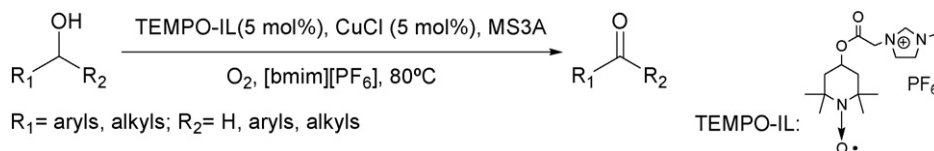
activated primary and secondary alcohols to the corresponding aldehydes and ketones in ionic liquid [bmim][PF₆] [17]. The products were isolated by a simple extraction with ether, and the ionic liquid can be recycled and reused. However, higher temperature and longer reaction time were required for the oxidation reactions in ionic liquid than those in ordinary organic solvents, and TEMPO cannot be reused.

In our recent work on the oxidation of organic compounds with molecular oxygen as terminal oxidant [18], we have found that some bases (for example, pyridine, *N*-methylimidazole, triethylamine) as co-catalyst in Gree's procedure could significantly promote the catalytic activity [19]. But the combination of catalyst system of CuCl/TEMPO/Base still has limitations. TEMPO and bases cannot be recycled and reused, and the separation of products from TEMPO and bases require lengthy workup procedures, especially when reactions are run on large scale.

Palladium-catalyzed aerobic oxidation of alcohols often benefits from the presence of molecular sieves [20,21]. But according to our knowledge CuCl/TEMPO catalyzed aerobic oxidation of alcohols in the presence of molecular sieves has seldom been reported in the literature. Therefore we studied the effects of Molecular sieve 3A (MS3A, a Brønsted base) on Gree's procedure and found a novel combination of catalyst system of CuCl/TEMPO-IL/MS3A (TEMPO-IL, ionic liquid immobilized TEMPO), which catalyzed the aerobic oxidation of alcohols in ionic liquid [bmim][PF₆] into aldehydes or ketones in high yields and selectivity (Scheme 1). Molecular sieve 3A was found to have a significant beneficial effect on the catalytic reactions. For example, the oxidation of cinnamyl alcohol was

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Scheme 1. MS3A promoted aerobic oxidation of alcohols catalyzed by CuCl/TEMPO-IL.

eight times faster in the presence of MS3A than that in the absence of MS3A. With TEMPO being immobilized on ionic liquid to form TEMPO-IL and the use of a heterogeneous promoter of MS3A, the catalyst system could easily be recycled and reused without loss in catalytic activity.

2. Experimental

TEMPO-IL was synthesized according to literature [22,23], SBA-15 was prepared according to literature [24,25]. Other chemicals were obtained from commercial resource and used without prior purification. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 equipped with a 30 m \times 0.32 mm \times 0.5 μm HP-Innowax capillary column and a flame ionization detector. Products were all known compounds and were identified by comparing of their physical and spectra data with those reported in the literature. Surface area was obtained basing on the BET method using the amount of N_2 adsorption at 77 K with a Micromeritics ASAP 2000 system.

2.1. Typical experimental procedure for oxidation of alcohols

Alcohol (5 mmol), TEMPO-IL (0.11 g, 0.25 mmol), CuCl (25 mg, 0.25 mmol) and MS3A (50 mg) were mixed with [bmim][PF₆] (3.5 mL) and stirred at 80 °C under O₂ (10 mL/min, 1 atm) for given time (Table 1). After completion, the mixture was extracted with ether (5 \times 10 mL) and analyzed by GC. The combined ether 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 or ketone which was characterized by ¹H NMR and IR analysis.

3. Results and discussion

3.1. Aerobic oxidation of alcohols promoted by MS3A

The CuCl/TEMPO-IL/MS3A catalytic system was applied to the oxidation of various types of benzylic, allylic, heterocyclic and aliphatic alcohols in ionic liquid [bmim][PF₆], and results are summarized in Table 1.

As shown in Table 1, all types of benzylic, allylic, heterocyclic and aliphatic alcohols, undergo oxidation into the corresponding aldehydes or ketones in ionic liquid [bmim][PF₆]. The reaction rate was remarkably faster in the presence of MS3A (Table 1, catalytic system A) than in the absence of it (Table 1, catalytic system B). Primary and secondary benzylic alcohols were converted to corresponding aldehydes and ketones with about 99% alcohol conversion and 80–94% product yield (Table 1, entries 1–8). Electron-rich and electron-deficient benzylic alcohols show no obvious difference. The rate of oxidation of cinnamyl alcohol was about eight times faster in the presence of MS3A than in the absence of it (Table 1, entries 9–10). Furfural alcohol was also converted into aldehyde in high yield in the presence of MS3A (Table 1, entries 11–12). Aliphatic alcohols, which were less reactive than benzylic and allylic alcohols under these systems, were oxidized to the corresponding aldehydes in prolonged reaction time with slightly higher conversion in

the presence of MS3A than in the absence of it. (Table 1, entries 13–16).

To optimize the conditions of oxidation, the influence of the amounts of MS3A on *p*-nitrobenzyl alcohol oxidation was studied by varying level from 0.01 to 0.15 g in 5 mmol substrate scale and maximum reaction rate was observed at 0.05 g (Fig. 1).

3.2. Recycling of the catalysts and ionic liquid

Extraction of the product with ether led to the separation of the catalyst system and ionic liquid from the product. The ionic liquid layer, which contains dissolved ionic liquid immobilized TEMPO (TEMPO-IL) and suspended CuCl and MS3A, was then distilled under vacuum to remove residual ether and water formed in the reaction and reused in next run for three times in the oxidation of *p*-nitrobenzyl alcohol with no loss in catalytic activity (Fig. 2).

3.3. Mechanistic aspects

In Uemura and co-workers' early work on Pd(II)-catalyzed aerobic oxidation of alcohols to aldehydes and ketones in the presence of MS3A [20,26,27], it was proposed that MS3A was responsible for the disproportionation of the hydrogen peroxide formed during reoxidation of Pd(0). Additionally, since water was formed upon disproportionation of the hydrogen peroxide, MS3A could also be responsible for sequestering the water [20]. However, Stahl and co-workers revealed that water did not have any inhibitory effect on the reaction rate, and by monitoring O₂ consumption, it was concluded that presence of MS3A slowed the disproportionation of hydrogen peroxide. According to these results, Stahl and co-workers attributed the accelerating effect of MS3A on Pd(II)-catalyzed aerobic alcohol oxidation to the Brønsted base property of MS3A [21].

To elucidate the role of MS3A in the catalyst system of CuCl/TEMPO-IL/MS3A, we studied the effects of water on the reac-

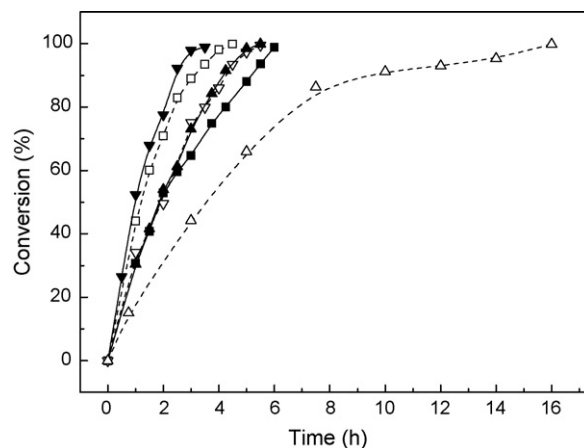
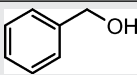
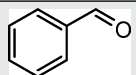
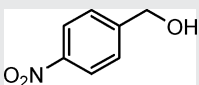
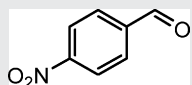
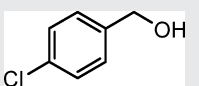
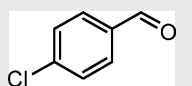
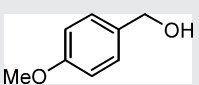
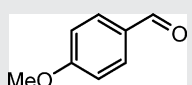
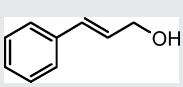
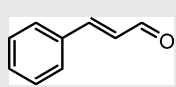
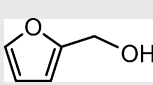
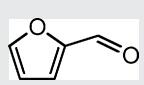
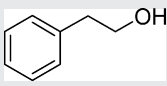
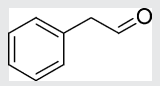


Fig. 1. Effects of the amounts of MS3A on the oxidation of *p*-nitrobenzyl alcohol. Reaction conditions: *p*-nitrobenzyl alcohol (5 mmol), CuCl (0.25 mmol), TEMPO-IL (0.25 mmol), MS3A and [bmim][PF₆] (3.5 mL), under O₂ at 80 °C; the mass of MS3A (■) 0.01 g, (□) 0.025 g, (▼) 0.05 g, (▽) 0.1 g, (▲) 0.15 g, (△) blank.

Table 1
Aerobic oxidation of alcohols

Entry	Alcohols	Products	Catalytic system ^a	Time (h)	Conversion ^b (%)	Yield ^c (%)
1			A	12	99	85
2			B	5	98	80
3			A	16	98	87
4			B	3	99	82
5			A	8	99	89
6			B	5	98	82
7			A	11	99	91
8			B	4.5	99	90
9			A	35	99	79
10			B	4.5	99	77
11			A	15	85	70
12			B	9.5	94	75
13			A	24	48	–
14			B	40	52	–
15	$n\text{-C}_{11}\text{H}_{23}\text{-CH}_2\text{OH}$	$n\text{-C}_{11}\text{H}_{23}\text{-CHO}$	A	30	60	–
16			B	48	63	–

^a Catalytic system A: CuCl/TEMPO-IL, B: CuCl/TEMPO-IL/MS3A.

^b GC conversion.

^c Isolated yield.

tions. MS3A was traditionally used as dehydrater, and water is a stoichiometric byproduct of aerobic oxidation reaction of alcohols [28]. It was reasonable to expect that MS3A improve the reactions by sequestering water in the oxidation of alcohols. However, the complete oxidation of 5 mmol alcohol would lead to the formation of 5 mmol (0.09 g) water. Considering only 0.05 g of MS3A was used, only about 20% of water would be absorbed by MS3A. Increase of the amount of MS3A used did not increase the reaction rate (Fig. 1).

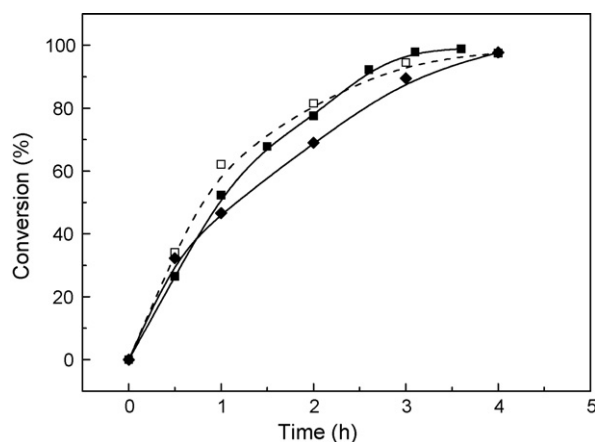


Fig. 2. Recycling of the catalysts and ionic liquid for the oxidation of *p*-nitrobenzyl alcohol. Reaction conditions: *p*-nitrobenzyl alcohol (5 mmol), CuCl (0.25 mmol), TEMPO-IL (0.25 mmol), MS3A (0.05 g) and [bmim][PF₆] (3.5 mL), under O₂ at 80 °C; (■) run 1, (□) run 2, (◆) run 3.

These results suggest that the accelerating effect of MS3A could not be attributed to sequestering of water in aerobic alcohol oxidation with the catalyst system of CuCl/TEMPO-IL/MS3A. In order to get more evidence to support this view, additional water was added to the catalytic system of CuCl/TEMPO-IL/MS3A and it was found that no obvious changes of the reaction rate and conversion were detected (Fig. 3).

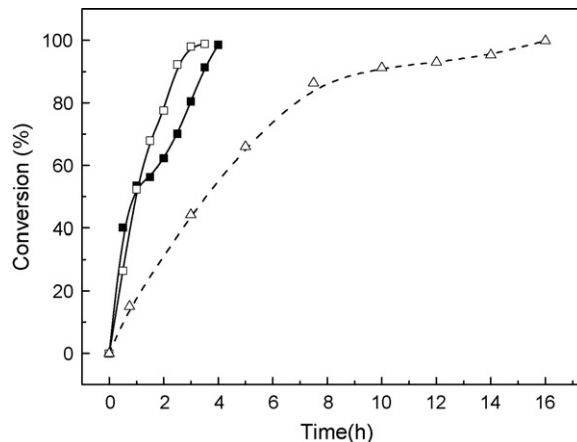


Fig. 3. Effects of water on the oxidation of *p*-nitrobenzyl alcohol. Reaction conditions: *p*-nitrobenzyl alcohol (5 mmol), CuCl (0.25 mmol), TEMPO-IL (0.25 mmol), MS3A and [bmim][PF₆] (3.5 mL), under O₂ at 80 °C; (■) 0.05 g MS3A, (□) 0.05 g MS3A and 0.05 g H₂O, (△) blank.

Table 2
Effects of types of molecular sieves on the oxidation of *p*-nitobenzyl alcohol^a

Molecular sieves	BET surface area (m ² /g)	Conversion ^b (%)
3A	540	99
HZSM-5	362	36
SBA-15	723	61
None	–	44

^a Reaction conditions: *p*-nitobenzyl alcohol (5 mmol), CuCl (0.25 mmol), TEMPO-IL (0.25 mmol), molecular sieves (0.05 g) and [bmim][PF₆] (3.5 mL), under O₂ at 80 °C, 3 h.

^b GC conversion.

According to our recent work, organic bases have beneficial effect on the aerobic alcohol oxidation with the catalytic system of CuCl/TEMPO. Therefore, we suppose that the accelerating effect of MS3A in the catalyst system of CuCl/TEMPO-IL/MS3A might be attributed to the Brønsted base property of MS3A similar to the effect of MS3A in the Pd(II) catalyzed oxidations of alcohols proposed by Stahl. To validate this postulate, the effects of three types of molecular sieves (MS3A, HZSM-5 and SBA-15) on the aerobic oxidation of *p*-nitobenzyl alcohol in the catalyst system of CuCl/TEMPO-IL/MS3A were compared (Table 2).

It could be seen from Table 2 that basic molecular sieve of MS3A and the neutral molecular sieve of SBA-15 could promote the aerobic oxidation of *p*-nitobenzyl alcohol. However, the presence of HZSM-5, an acidic molecular sieve, decreases the catalytic activity. The basic property of molecular sieves seems to be major reason for accelerating the aerobic oxidation of alcohols to aldehydes and ketones with the catalyst system of CuCl/TEMPO-IL/MS3A. The moderate effect of the neutral molecular sieve of SBA-15 on the reaction might be attributed to its large BET surface area.

4. Conclusion

In summary, an efficient and selective aerobic oxidation procedure of alcohols to the corresponding aldehydes or ketones using CuCl/TEMPO-IL/MS3A catalytic system in ionic liquid [bmim][PF₆] has been developed. MS3A serves as a heterogeneous Brønsted base to enhance the reaction rate remarkably. It is noteworthy to men-

tion that the catalysts and solvent could easily be recycled and reused without loss of activity. The scope and synthetic and industrial applications of the oxidation procedure are currently under investigation.

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