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Heterogeneous Cu–Mn oxides mediate efficiently TEMPO-catalyzed aerobic oxidation of alcohols

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Cu–Mn oxides in combination of 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO) were firstly used to catalyze aerobic selective oxidation of alcohols to carbonyl compounds. Such recyclable heterogeneous cocatalysts showed good catalytic performance in the process when the molar ratio of Cu and Mn is over 1.

KEY WORDS: Cu-Mn Oxides; TEMPO; catalysis; aerobic oxidation; alcohols.

1. Introduction

The aerobic selective oxidation of alcohols to the corresponding aldehydes and ketones has received great attention, since this important functional group transformations were applied widely both in fundamental synthesis research and industrial manufacturing, and the use of molecular oxygen as terminal oxidant is of economic and environmental benefits [1]. A variety of catalysts and catalytic systems, including homogeneous and heterogeneous type, have been developed for selective aerobic oxidation of alcohols [2, 3]. Among them, 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO) is particularly attractive because such small-molecule organocatalyst exhibited very high efficiencies and selectivities in many case of oxidation of alcohols [4]. The mechanism of TEMPO-catalyzed oxidation of alcohols has been ascribed to that the *in situ* formed oxammonium cation from TEMPO effectively and selectively oxidize alcohol to the corresponding aldehydes and ketones, and itself converts to 2,2,6,6-tetramethyl-1-hydroxypiperidine (TEMPOH) [5]. Thus, the transformation of TEMPO and/or TEMPOH to oxammonium cation plays a pivotal role in TEMPO-catalyzed oxidation of alcohol. In the case of the oxidation of alcohols using molecular oxygen as the terminal oxidant, actually, the one-electron oxidation transformation between TEMPO or TEMPOH and oxammonium cation always need the assistance of cocatalysts via a multistage catalytic reaction cascade. Most efforts has been paid in the last few years to develop homogeneous cocatalysts, such as, $NaNO_2/Br_2$ [6], $NaNO_2$/1,3-dibromo-5,5-dimethylhydantoin [7], [bis(acetoxy)iodo]benzene/KNO_2 [8], $Mn(NO_3)_2/Co(NO_3)_2$ or $Mn(NO_3)_2/Cu(NO_3)_2$ in acetic acid [9], CuCl in DMF [10], $CuBr\cdot Me_2S$ under fluorous biphasic condition [11], $CuBr_2$(2,2′-bipyridine)/*t*-BuOK [12], $RuCl_2(PPh_3)_3$ [13], and CH_3ReO_3/HBr in acetic acid [14], etc. However, as far as we are aware, there is no report on TEMPO-catalyzed oxidation of alcohol by molecular oxygen with heterogeneous cocatalysts.

Recently S. Cicchi et al reported that manganese dioxide could stoichiometrically oxidize hydroxylamines to the corresponding nitrones with good to excellent yields even in an ice-cooled solution [15]. Furthermore, various metal oxides in various forms, such as single- and multi-component, immobilized on supports etc, have been employed as oxidation catalyst [16, 17], which are easily prepared, simple to use and capable of being recycled. These inspired us that metal oxides could *in situ* oxidize TEMPO and/or TEMPOH to oxammonium cation, and then serve as heterogeneous cocatalysts for TEMPO-catalyzed aerobic oxidation of alcohol. In this report, MnO_2, CuO, and Cu–Mn mixed oxides prepared by a co-precipitation method, were applied firstly to mediate efficiently TEMPO-catalyzed aerobic selective oxidation of a variety of alcohols to the corresponding aldehydes and ketones under neutral condition, and such non-noble metal oxide cocatalyst are low cost, environmentally friendly and relatively highly active, as well as halogen-free.

2. Experimental

2.1. *Preparation of metal oxides*

The preparation of active MnO_2 accorded to the typical procedures in literature [18]. To a solution of $MnSO_4$ (10 g in H_2O 190 ml), a solution of $KMnO_4$ (7 g in 133 ml H_2O) was added at 60 °C under stirring. After the suspension was stirred at 60 °C for 1 h, the

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precipitate was filtered and washed with water until free of sulfate ions. The precipitate was dried to constant weight at 60 °C, then triturated and sifted from a 140 mesh sieve, yielded dark-brown powder. Its XRD pattern was indexed to amorphous MnO_2. MnO_2 in the grade of spectral purity (SP MnO_2), MnO_2 in the grade of analytical purity (AR MnO_2), and CuO in the grade of analytical purity were purchased from Tianjin Kermel Chemical Regent Development Center. Natural Pyrolusite powder with an 89 wt% content of MnO_2 was purchased from Qingchong Corp. Ltd., Hunan, China.

All the Cu–Mn mixed oxides cocatalysts used in this study were prepared by a coprecipitation method, which is described typically with 1:1 mol ratio of Cu and Mn as follows. The pre-mixed aqueous solution of copper sulfate ($CuSO_4 \cdot 5H_2O$) (0.33 mol l^{-1}) and manganese sulfate ($MnSO_4 \cdot H_2O$) (0.33 mol l^{-1}) was continuously added to 150 ml aqueous NaOH solution (1.3 mol l^{-1}), and stirred for additional 1 h. The precipitate was first filtered and then washed several times with warm distilled water until no further SO_4^{2-} was detected in the washings. The cake was dried at 120 °C for 5 h and calcined at 450 °C for 4 h. After trituration, the final catalyst was sifted from a 140 mesh sieve. The catalysts is denoted as Cu_xMn_y, where x:y represents the molar ratio of copper and manganese. XRD patterns indicated CuMn was assigned to spinel oxide $Cu_{1.5}Mn_{1.5}O_4$. While x:y < 1, Mn_2O_3 and spinel oxide $Cu_{1.5}Mn_{1.5}O_4$ existed together. CuO and spinel oxide $Cu_{1.5}Mn_{1.5}O_4$ existed together in the case of x:y > 1.

2.2. Catalytic oxidation tests

The reaction was carried out in a 70-ml Teflon-lined autoclave and general procedure is described typically with benzyl alcohol as follows: a mixture of TEMPO (302 mg, 10 mol%), metal oxide cocatalyst (10 wt%), benzyl alcohol (2 ml, 19.3 mmol), and dichloromethane (10 ml) was stirred and heated to 120 °C after the atomsphere over the mixture was replaced with O_2 for three times. The pressure of O_2 was kept at 0.4 MPa for the desired reaction time. After the reaction mixture was cooled to room temperature, 20 ml ethanol was added. Then the cocatalyst was separated by filtration, and ethanol solution was analyzed by gas chromatography.

Gas chromatography measurements were conducted using an Agilent Technologies 6890N Network GC System with a flame ionization detector and a DB-1 capillary column (30 m × 0.535 mm × 3.0 μm). Agilent Chemstation software was used for spectra acquisition and processing. The conversions and selectivities were determined by GC area normalization.

3. Results and discussion

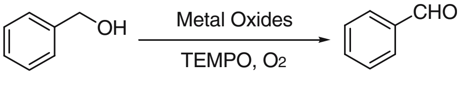
Initially, the aerobic oxidation of benzyl alcohol to benzaldehyde in CH_2Cl_2 at 80 °C was employed as the model reaction for investigating catalysis of various metal oxides in combination with TEMPO. The results are shown in table 1.

It is known that for organic synthesis MnO_2 is a useful selective oxidizing reagent, which is always required over fivefold weight of active MnO_2 on organic substrates [18]. During our catalytic oxidation of alcohol in a certain term of 6 h, 10 mol% of active MnO_2 alone realized 23.5% conversion with 100% selectivity of benzaldehyde (entry 5 in Table 1), which accords with the feature of MnO_2-oxidation. When 10 mol% TEMPO and 10 mol% of active MnO_2 were used together at the same conditions, the 100% selectivity at 32.3% conversion could be obtained (entry 4 in Table 1). As expected, these results clearly indicated the combination of active MnO_2 and TEMPO can selectively catalyzed aerobic oxidation of alcohol. Some commercially available types of MnO_2 were also tested. SP MnO_2, AR MnO_2 and nature MnO_2 realized 14.4%, 12.9%, and 1.6% conversions, respectively. As a conclusion, as-prepared active MnO_2 is superior to the other types of MnO_2 in mediation of TEMPO-oxidation.

Some copper salts and complexes were found to efficiently mediate TEMPO-oxidation of alcohol even under mild conditions [9–12], however, strong polar, acidic or fluorous solvents was always required for homogeneous reaction. It is notable the fact that the formation of the oxammonium cation by disproportionation of TEMPO in the acidic medium will promote effectively TEMPO-catalysis [9]. In our study, with CH_2Cl_2 as solvent under neutral condition, simple CuO gave a 34.0 % conversion of benzyl alcohol at 80°C, nearing to 32.3 % conversion of active MnO_2. The relatively lower selectivity than that of MnO_2 probably arise from CuO oxidize a small quantity of benzaldehyde further to benzoic acid. But at 120°C CuO gave a much higher conversion (77.5%) than active MnO_2 (38.4 %).

Many investigations have revealed that the catalytic activity of metal oxide often be promoted by synergism of incorporated other metal oxide [17,, 20]. In particular, catalysts based on Cu–Mn mixed oxides are of considerable industrial interest owing to their activity as oxidation catalysts [21, 22]. Therefore, various Cu–Mn mixed oxides with different molar ratios of Cu and Mn were prepared by a co-precipitation method, and were employed in aerobic TEMPO-oxidation of benzyl alcohol. 31.3% conversion of Cu_2Mn (the molar ratio of Cu and Mn is 2) is near to active MnO_2 and CuO at 80 °C. However, Cu_2Mn showed a higher catalytic activity at 120 °C, giving 98.8% conversion with 98.3% selectivity. Cu_xMn_y with different molar ratio of Cu and Mn displayed different catalytic results. Cu_xMn_y showed lower catalytic activities when the content of Cu is less than Mn; when Cu contents is more than Mn, such as Cu_2Mn, Cu_3Mn, Cu_4Mn and Cu_5Mn, Cu_xMn_y can

Table 1
Oxidation of benzyl alcohol using various metal oxides and TEMPO[a]



Entry	Metal Oxides	Temperature (°C)	Conversions (%)	Selectivities(%)
1	AR MnO_2	80	12.9	100
2	SP MnO_2	80	14.4	100
3	Nature MnO_2	80	1.6	100
4	Active MnO_2	80	32.3	100
5	Active MnO_2	120	38.4	100
6[b]	Active MnO_2	80	23.5	100
7	CuO	80	34.0	93.0
8[b]	CuO	80	0.4	100
9	CuO	120	77.5	98.6
10	Cu_2Mn	80	31.3	94.6
11	Cu_2Mn	100	38.9	96.3
12	Cu_2Mn	120	98.8	98.3
13	CuMn	120	62.6	97.5
14	$CuMn_2$	120	33.6	95.6
15	$CuMn_4$	120	31.1	92.4
16	Cu_3Mn	120	98.5	98.5
17	Cu_4Mn	120	98.7	99.4
18	Cu_5Mn	120	98.7	98.7
19[b]	Cu_2Mn	120	3.2	100

[a] Reactions were carried out using 2 ml benzyl alcohol (19.3 mmol), 10 mol% of TEMPO, 10 mol% of metal oxides and 10 ml dichloromethane under 0.4 MPa O_2 for 6 h.

[b] TEMPO-free.

mediated efficiently TEMPO-catalyzed aerobic oxidation of benzyl alcohol, both of conversions and selectivities exceeded 98%.

The recycle tests were conducted with Cu_2Mn in order to investigate the recyclability of the Cu–Mn oxide cocatalysts. After the reaction, the Cu_2Mn was filtered and washed with ethanol for several times, then dried at 100 °C for 4 h to remove ethanol and used together with TEMPO for another reaction. After the three runs, both of the conversions and selectivities remained at the similar level of the first run. Cu_2Mn without any appreciable loss of activity in the recycle tests can be proved to stable structure during catalysis, and recyclable.

The Cu_2Mn/TEMPO were further employed to catalyze aerobic oxidation of various alcohols (Table 2). As it was shown, excellent conversions were obtained when benzylic alcohols and cinnamyl alcohol were used. In TEMPO-catalysis, secondary alcohols react generally slower than primary especially in the case of copper compounds as cocatalysts [10–12]. In our study, no reaction is observed with benzhydrol probably because of steric hindrance. The oxidation of 4-hydroxybenzyl alcohol at 120 °C for 6 h only gave 53.9% conversion, quite lower than other benzylic alcohols. Prolonging to 10 h, the conversion increased to 96.8%, but the selectivity of 4-hydroxybenzaldehyde decreased. Unfortunately, the oxidation of hydroxyl at aliphatic moiety proceeded smoothly.

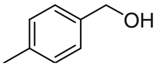
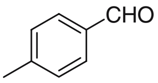
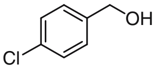
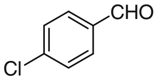
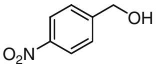
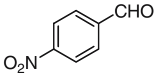
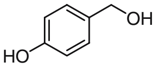
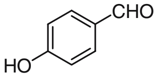
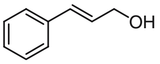
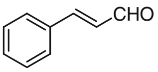
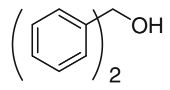
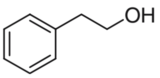
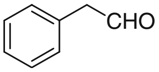
The redox catalyst containing Cu and/or Mn depends on the reduction of metal species of higher valence to lower, and oxidation of the lower to the higher by dioxygen [4, 10, 16, 19]. Therefore, the catalytic mechanism of MO_x/ TEMPO is proposed (Scheme 1), which encompasses a two-stage catalytic reaction cascade: the cycle between TEMPOH and oxammonium cation, and the cycle between Mn^{n+} and $Mn^{(n-1)+}$. Oxammonium cation oxidizes alcohol to the corresponding carbonyl compounds, and returns to TEMPOH. Mn^{n+} regenerates from $Mn^{(n-1)+}$ by dioxygen oxidation. The better performance of Cu-Mn mixed oxides was suggested coming of the synergic effect between Cu and Mn.

4. Conclusions

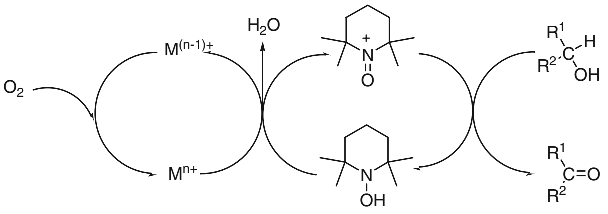
In conclusion, this paper firstly developed metal oxides can serve as heterogeneous co-catalysts mediating TEMPO-catalyzed aerobic selective oxidation of alcohols. Cu_xMn_y (the molar ratio of Cu and Mn is over 1) prepared by a co-precipitation method were highly active. Although further studies on characterizations and detail mechanism are currently underway, such recyclable non-noble heterogeneous co-catalysts display low-cost, environmentally

Table 2

Cu_2Mn / TEMPO catalyzed oxidation of various alcohols[a]

Entry	Alcohol	Product	Time (h)	Conversions (%)	Selectivities (%)
1			8	98.4	99.4
2			8	98.9	99.7
3			6	99.7	99.5
5			10 6	96.8 53.9	82.2 98.6
6			6	99.7	99.5
7		–	6	0	–
8			6 16	9.6 58.9	93.5 83.5

[a]The reactions were carried out under 0.4 MPa of O_2 at 120 °C in 10 ml of CH_2Cl_2; the used amounts of solid substrates were 2 g and liquid were 2 ml; 10 mol% of TEMPO and 10 wt% of Cu_2Mn were used in all case.



Scheme 1. Suggested catalytic cycle of MO_x/ TEMPO system in aerobic oxidation of alcohol.

friendly, and halogen-free features for TEMPO-catalyzed aerobic oxidation of alcohols.

Acknowledgments

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