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Recyclable Carbon Supported Copper-Manganese Oxide for Selective Aerobic Oxidation of Alcohols in Combination with 2,2,6,6-Tetramethylpiperidyl-1-oxyl under Neutral Condition

Guanyu Yang,[a,*] Weimin Zhu,[a] Panke Zhang,[a] Huazhen Xue,[a] Wei Wang,[a] Junshan Tian,[a] and Maoping Song[a,*]

[a] Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China
Fax: (+86)-371-6776-3927; e-mail: yangguanyu@zzu.edu.cn

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Abstract: Due to the promotion of the surface area and the dispersion of active components upon supporting mixed metal oxides on the porous material active carbon, the copper-manganese oxide on carbon system has been proven to be much more efficient than the co-precipitation prepared Cu-Mn oxide in mediating the 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO)-catalyzed aerobic oxidation of alcohols. Even at 30 °C and with a 0.1 mol% load of TEMPO, the oxidations proceeded smoothly. Upon catalysis with the Cu-Mn oxide/C (10 wt%) and TEMPO (0.5–5 mol%), various alcohols were oxidized selectively to the corresponding aldehydes or ketones with molecular oxygen at 80 °C. Such a stable, recyclable heterogeneous cocatalyst permits alcohols to be oxidized under neutral and mild conditions.

Keywords: aerobic oxidation; alcohols; carbon; catalysis; copper-manganese mixed oxide; 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO)

The transformation of alcohols to the corresponding aldehydes or ketones is of importance in fundamental research and industrial manufacturing.[1] Many catalytic systems have been discovered for using molecular oxygen as environmentally friendly oxidant for the selective oxidation of alcohols.[2] Of particular interest are the catalytic systems using 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) as a key catalyst[3] in combination with various homogeneous multicomponent cocatalytic systems, such as, *tert*-butyl nitrite/HBr,[4] $NaNO_2/FeCl_3$,[5] $NaNO_2/Br_2$,[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] $CuBr_2$(2,2′-bipyridine)/*t*-BuOK,[10] $RuCl_2(PPh_3)_3$,[11] $CuBr{\cdot}Me_2S$,[12] CH_3ReO_3/HBr in acetic acid,[13] Cu(II)-diimine complexes,[14] etc. These multicomponent cocatalytic systems build one (or more) redox bridge(s) between molecular oxygen activation and *in situ* oxidation of TEMPO to its oxammonium cation, which is the real oxidant for the selective oxidation of alcohols. However, these homogeneous cocatalysts are difficult to recover and are often discarded in the waste water; also the acidic reaction conditions and the use of halides tend toward potential equipment corrosion in industrial applications.

Growing attention is being given to developing heterogeneous catalysts for alcohol oxidation because of their simple separability and recyclability, which are of significant industrial interest.[15] Based on the assumption that the redox-active heterogeneous material could promote the transformation of TEMPO to its oxammonium cation, we found that co-precipitation prepared Cu-Mn mixed oxides (the molar ratio of Cu and Mn over 1) are recyclable heterogeneous cocatalysts for TEMPO-catalyzed aerobic oxidation of alcohols under neutral condition,[16] avoiding the usage of acidic solvents and halogen-containing cocatalyst. In continuation of our study on this subject with consideration of the fact that the porous material could promote the surface area and the dispersion of active components, as well as the activity of catalyst, we are particularly interested in exploring the potential of the supported Cu-Mn oxide. Herein, we report on the aerobic oxidation of alcohols by a coupled system of the Cu-Mn mixed oxide supported on active carbon and TEMPO.

The Cu-Mn oxide/C catalyst was prepared using the incipient wetness method according to the literature.[17] The commercial active carbon (5.0 g, 60–80 mesh, sorption capacity 1.4 mL g^{-1}) was impregnated with an aqueous solution of copper nitrate (3 mmol) and manganese nitrate (1 mmol), and then was dried at 115 °C. Finally, the Cu-Mn oxide/C catalyst was obtained by calcination in a vacuum quartz tube at 400 °C in flowing N_2 for 4 h.

In the initial tests on the aerobic oxidation of benzyl alcohol, it was encouraging that the carbon supported Cu-Mn oxide (10 wt%) in combination with TEMPO (5 mol%) gave 90.9% conversion of benzyl alcohol with $>$ 99% selectivity for benzaldehyde at 80 °C under 0.4 MPa O_2 for 6 h (entry 7, Table 1), and thus exhibited a much better catalytic performance than the coprecipitation prepared Cu-Mn mixed oxide with the same molar ratio of Cu and Mn which realized merely 31.4% conversion under the same conditions. On the other hand, no peak of active components was found in the XRD pattern of the Cu-Mn oxide/C catalyst (see Supporting Information). This implied, as expected, that the catalytic activity of the Cu-Mn mixed oxide could be promoted by supporting it on a porous material due to the increase of the surface area of the catalyst and the dispersion of the active components.

The optimal catalytic results for the benzyl alcohol oxidation using the coupled system of the Cu-Mn oxide/C and TEMPO are displayed in Table 1. As can be seen, the coupled system can work even at as low as 30 °C, giving *ca.* 54% conversions in the course of 6 h (entry 1 and 2, Table 1). Increasing the temperature increased the reaction rate, and 80 °C seemed to be the preferable temperature. The pressure of molecular oxygen shown a positive influence on the rate below 0.6 MPa, but above 0.6 MPa it lost its effect. This suggests that the rate of oxidation is controlled by molecular oxygen diffusing inside the Cu-Mn oxide/C under the lower presure. However, under 0.4 MPa at 80 °C the oxidation of benzyl alcohol to benzaldehyde still reached a near quantitative result on prolonging the reaction time to 12 h (entry 13, Table 1). So 0.4 MPa of molecular oxygen was chosen in the further optimal test. It was not unexpected to find that the more loading amounts of both the Cu-Mn oxide/C and TEMPO result in faster rates of oxidation (entries 14–20, Table 1). However, the influence of the loading amount of the Cu-Mn oxide/C on the rate was obviously stronger than that of TEMPO. In the course of 6 h, 1 mol% TEMPO and 10 wt% Cu-Mn oxide/C realized 98.9% conversion (entry 19, Table 1), but 1 wt% Cu-Mn oxide/C and 5 mol% TEMPO gave only 14.2% conversion (entry 16, Table 1). These mean that the oxidation rate depends on the reactants diffusing to the catalytic sites on the Cu-Mn oxide/C because the oxidation occurs on the intrasurface of solid catalyst. Decreasing the load amount of TEMPO to 0.5 mol% and 0.1 mol% in combination with 10 wt% Cu-Mn oxide/C, the oxidation realized 80.1% and 48.2% conversion, respectively (entry 21 and 22, Table 1). Prolonging the time to

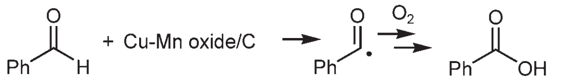
Table 1. Aerobic oxidation of benzyl alcohol to benzaldehyde by the Cu-Mn oxide/C and TEMPO.[a]

Entry	Cu-Mn oxide/C [wt%]	TEMPO [mol%]	T [°C]	P [MPa]	Time [h]	Conversion [%]	Selectivity [%]
1	10	5	30	0.4	6	54.6	90.4
2	10	5	30	0.8	6	54.2	92.9
3	10	5	40	0.8	6	64.8	93.9
4	10	5	60	0.8	6	87.3	$>$99
5	10	5	80	0.8	6	98.8	$>$99
6	10	5	100	0.8	6	99.0	$>$99
7	10	5	80	0.4	6	90.9	$>$99
8	10	5	80	0.6	6	98.8	$>$99
9	10	5	80	1.0	6	98.8	$>$99
10	10	5	40	0.4	18	82.6	93.0
11	10	5	80	0.4	3	81.3	$>$99
12	10	5	80	0.4	6	90.9	$>$99
13	10	5	80	0.4	12	99.0	$>$99
14	5	5	80	0.4	6	41.5	$>$99
15	3	5	80	0.4	6	27.4	$>$99
16	1	5	80	0.4	6	14.2	$>$99
17	10	3	80	0.4	6	100	$>$99
18	10	3	80	0.4	3	87.6	$>$99
19	10	1	80	0.4	6	98.9	$>$99
20	10	1	80	0.4	3	79.5	$>$99
21	10	0.5	80	0.4	6	80.1	$>$99
22	10	0.1	80	0.4	8	48.2	$>$99
23	10	0.5	80	0.4	24	97.9	$>$99
24	10	0	80	0.4	6	1.6	-

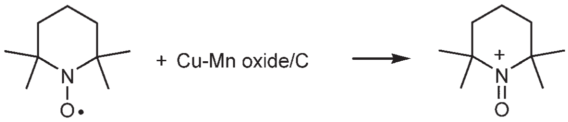
[a] The oxidations were carried out using 2 mL benzyl alcohol and 10 mL CH_2Cl_2 in all cases.

24 h increased the conversion to 97.7% in the case of 0.5 mol% TEMPO (entry 23, Table 1) and 96.1% isolated yield was obtained. These showed that the low load of TEMPO still has significant catalytic activity.

As can be seen in Table 1, the selectivities for benzaldehyde were all above 99% when the reaction temperatures were above 60 °C, but it was surprising that below 60 °C the selectivities were out of line, and a small amount of benzoic acid always existed in the oxidations (entries 1–3 and 10, Table 1). It is known that benzaldehyde could be oxidized easily to benzoic acid by molecular oxygen in long-term storage following the radical mechanism, and aldehydes are often used as the radical initiator.[18] Therefore, the contrast tests were conducted using benzaldehyde as the substrate instead of benzyl alcohol. Employing the Cu-Mn oxide/C (10 wt%) alone, benzaldehyde was converted completely to benzoic acid under 0.4 MPa O_2 within 6 h at 30 °C, 40 °C and 60 °C, respectively. This shows us that the Cu-Mn oxide/C has the ability to catalyze a one-electron oxidation. Hence, we suggested that two competitive reactions [see the reactions of Eq. (1) and Eq. (2)] occurred on the Cu-Mn oxide/C. The oxidation of TEMPO to its oxammonium cation [Eq. (2)] takes place more easily than the aerobic oxidation of benzaldehyde [Eq. (1)]. This is why all oxidations of benzaldehyde using the Cu-Mn oxide/C (10 wt%) and TEMPO (5 mol%) together gave as low as *ca.* 6% conversions under 0.4 MPa O_2 for 6 h at temperatures of 30 °C and 40 °C, respectively. Above 60 °C the reaction of Eq. (2) becomes so fast that Eq. (1) has little chance to ocurr, so benzaldehyde is the sole product in catalytic oxidation of benzyl alcohol.



(1)



(2)

Nitrites are often used as a component of the catalytic system in the TEMPO-catalyzed aerobic oxidation of alcohols, which activate molecular oxygen and transfer its oxidizability to next component or TEMPO.[5–8] However, addition of $NaNO_2$ or $NaNO_2$/acetic acid into the system of the Cu-Mn oxide/C and TEMPO did not afford any evident improvement in the catalytic activity. It could be that molecular oxygen oxidized directly a metal species of lower valence to a higher one after the reaction of Eq. (2) had occurred, and then the constructed redox cycle of the Cu-Mn oxide/C proceeded according to what we had documented before.[16]

The recycle tests were conducted in order to investigate the recyclability of the Cu-Mn oxide/C. After the reaction, the Cu-Mn oxide/C was filtered and washed with ethanol several times, dried at 100 °C for 4 h to remove the ethanol, and then used together with TEMPO for another reaction. After five runs, both of the conversions and the selectivities remained at similar levels to that of the first run. The Cu-Mn oxide/C without any detectable loss of activity in the recycle tests thus proves to be stable during catalysis, and recyclable.

The coupled system was employed further to catalyze the aerobic oxidation of various alcohols (Table 2). It is a general phenomenon that the oxidations of secondary alcohols and aliphatic alcohols proceed slowly when Cu compounds and TEMPO are used as catalysts.[14,19] The combination of the Cu-Mn oxide/C and TEMPO cannot overcome this hurdle. In the presence of 10 wt% Cu-Mn oxide/C and 5 mol% TEMPO under 0.4 MPa at 80 °C for 8–10 h, the oxidations of 1-phenethanol, 2-phenethanol, 1-heptanol and 2-heptanol gave 43.3%, 12.7%, 23.8% and 12.5% conversions, respectively (entries 9–12, Table 2). However, the oxidations of cinnamyl alcohol and all primary benzylic alcohols with either electron-donating or electron-withdrawing substituents can be catalyzed efficiently, among which (4-nitrophenyl)methanol behaves almost perfectly, realizing 100% conversion and 99.0% isolated yield. Even with as low as 0.5 mol% load of TEMPO, these alcohols can be oxidized nearly completely to their corresponding aldehydes by merely prolonging the reaction time.

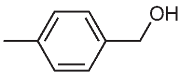
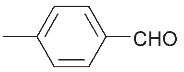
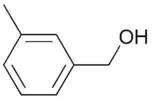
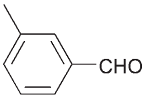
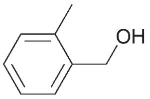
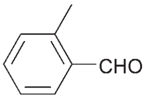
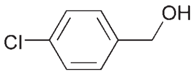
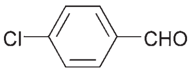
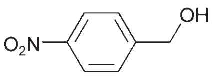
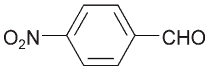
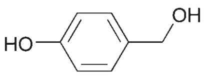
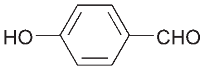
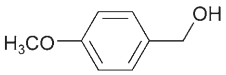
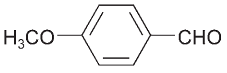
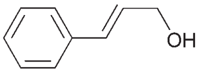
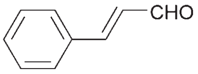
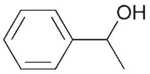
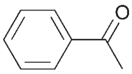
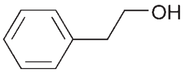
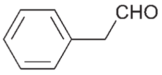
In summary, we have found that the supported Cu-Mn oxide/C system is a heterogeneous cocatalyst that can activate directly molecular oxygen and transfer its oxidizing power to the oxidation of TEMPO. As a result, the coupled catalytic system of Cu-Mn oxide/C and TEMPO has been developed for the aerobic selective oxidation of various alcohols to the corresponding aldehydes or ketones. It works efficiently at 80 °C, and the TEMPO load can be decreased to as low as 0.5 mol%. The easy handling, simple separation and reusability of such a heterogeneous cocatalyst enable the oxidation to be conducted under neutral condition, and is of significant industrial interest.

Experimental Section

General Remarks

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

Table 2. Aerobic oxidations of various alcohols by the Cu-Mn oxide/C and TEMPO.[a]

Entry	Substrate	TEMPO [mol%]	Time [h]	Conversion [%]	Product	Selectivity [%]
1		5 0.5	1 24	93.1 100		>99 >99
2		3 0.5	3 16	97.7 97.9		>99 >99
3		3 0.5	3 16	87.7 82.4		>99 >99
4		5 3 0.5	2.5 2.5 24	96.9 86.0 100		>99 >99 >99
5		5 3 0.5	2 2 12	100 100 100		>99 >99 >99
6		5 3	3.5 3.5	83.8 75.4		>99 >99
7		3 0.5	3 16	98.7 94.6		>99 >99
8		5 3	2 2	97.7 97.7		>99 >99
9		5	8	43.3		>99
10		5	8	12.7		>99
11	1-heptanol	5	10	23.8	heptanal	>99
12	2-heptanol	5	10	12.5	2-heptanone	>99

[a] The reactions were carried out under 0.4 MPa of O_2 at 80 °C in 10 mL of CH_2Cl_2; the used amounts of solid substrates were 2 g and those for liquid substrates were 2 mL; 10 wt% of the Cu-Mn oxide/C were used in all case. The conversions and the selectivities are based on GC with area normalization.

was used for spectra acquisition and processing. The conversions and the selectivities were determined by GC area normalization. All starting materials and catalysts were purchased from commercial sources and used without further treatment.

General Typical Procedure for the Oxidation

The reaction was carried out in a 70-mL autoclave and the general procedure is described typically with benzyl alcohol as follows: a mixture of TEMPO (151 mg, 5 mol%), Cu-Mn oxide/C (10 wt%), benzyl alcohol (2 mL, 19.3 mmol), and dichloromethane (10 mL) was stirred and heated to 80 °C after the atmosphere 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 had cooled to room temperature, 20 mL ethanol were added. Then the cocatalyst was separated by filtration, and ethanol solution was analyzed by gas chromatography.

The isolation procedure for the oxidation products benzaldehyde and *p*-nitrobenzaldehyde were conducted as follows: after the GC measurement, the ethanol solution of the reaction mixture was removed under reduced pressure, and then the residue was purified by silica-gel column chromatography, EtOAc/hexane (v:v = 1:2) used as eluant to afford the corresponding aldehyde product.

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