ORIGINAL PAPER



Allylic oxidation of cyclic alkenes with molecular oxygen and *tert*butyl hydroperoxide over copper-manganese oxides

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Received: 12 January 2016/Accepted: 15 March 2016 © Springer-Verlag Wien 2016

Abstract An efficient and mild method for the allylic oxidation of cyclic alkenes employing molecular oxygen and *tert*-butyl hydroperoxide as the oxidant, copper-manganese oxides as heterogeneous catalyst under ambient temperature is proposed. The catalyst, which was prepared by co-precipitation and characterized, was evaluated oxidation of isolongifolene as a typical mode substrate. The catalyst showed a good catalytic activity and remained nearly the same after four cycles. The scope of the reaction was investigated with a variety of cyclic alkenes compounds.

Graphical abstract



Keywords Oxidation · Heterogeneous catalysis · TBHP · Isolongifolene · Chemoselectivity

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Introduction

The allylic oxidation of olefins into value-added α,β -unsaturated carbonyl compounds or alkenyl alcohol compounds are a fundamental transformation in organic synthesis and industrial chemistry [1]. Allylic oxidation of 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-2H-2,4a-methanonaphthalene(isolongifolene) to 1,2,3,4,5,6-hexahydro-1,1,5,5-tetramethyl-7H-2,4a-methanonaphthalen-7one (isolongifolenone) is of interest because isolongifolenone and its derivatives have been found to be active against tyrosinase and antimalarial. In addition, isolongifolenone also be found more effective than Deet in repelling ticks [2] and deterring feeding mosquitoes [3, 4]. Classically, allylic oxidation mainly with SeO_2 [5–7], MnO₂ [8], potassium permanganate [9], chromium hexacarbonyl [10], and Pd compounds [11–14] frequently encounters problems such as toxicity, high cost, and low regioselectivity.

The use of *tert*-butyl hydroperoxide (TBHP) in combination with some of the reagents such as inorganic metal [15–17], diacetoxyiodobenzene [18], Schiff base complexes [19–21], metal organic frameworks (MOFs) [22, 23] has afforded allylically oxidized products but the reaction still utilizes the toxic compound, and the process produces hazardous waste making the process eco unfriendly.

Cu-based oxide catalysts [24–27] that are highly desirable objects for the allylic oxidation due to their good catalytic performances and low fabrication costs could become an alternative to the precious metal catalysts. Manganese(III) acetate catalyzed [28] allylic oxidation of alkenes to the corresponding enones also showed appreciable regioselectivity and chemoselectivity. Against this background, it is interesting to consider the influence of copper-manganese oxides catalysts for allylic oxidation of alkenes.



Mixed manganese-copper oxides are well known as active catalyst for the oxidation of CO to CO_2 [29]. Mixed copper-manganese oxides as catalyst have also been studied for the oxidation toluene [30], for the oxidation of benzyl alcohol to benzaldehyde with molecular oxygen [31], for ozone decomposition [32], NO reduction [33], and other redox processes. However, to date, mixed coppermanganese oxides (here after called Cu–Mn Ox) catalysts have not been studied for allylic oxidation of alkenes.

In this work, we have synthesized mixed copper-manganese oxides catalyst by simple co-precipitation method and have examined its catalytic property for allylic oxidation of alkenes with molecular oxygen and TBHP as the oxidant (Scheme 1).

Results and discussion

Element, surface area, and porosity measurements analysis

The results of the ICP analysis of the prepared Cu–Mn Ox in Table 1 show that a content of the Cu–Mn Ox was close to that of the molar ratio is approximately 0.40. While there still exists in slight differences, it could be possibly that some part of the ions are not precipitated, and remain in solution. In addition, [Mn]/([Cu] + [Mn]) mole ratios of recycled Cu–Mn solids material decline to 0.39 from 0.41 in fresh Cu–Mn Ox. It may be mainly due to the amount of copper loss in catalytic oxidation reaction. The adsorptive and microstructural properties of the Cu–Mn Ox were

evaluated from low temperature (77 K) static nitrogen physisorption-desorption isotherms by a volume method using a Micromeritics ASAP2020 M surface/porosity analyzer. The surface area and pore volume of fresh and recycled Cu–Mn Ox (673 K) were determined by the BET method (Table 1). The fresh Cu–Mn Ox shows a lager specific surface area (59.69 m²/g) and total pore volume (0.45 cm³/g) followed by the recycled Cu–Mn Ox (33.38 m²/g and 0.23 cm³/g). Average pore diameters of fresh and recycled catalysts are 27.86 and 28.21 nm, respectively. The results obtained show that samples possess a larger specific surface area and narrow pore volume compared with the reports by Ivanets [34].

Fourier transform infrared

The FT-IR spectra of fresh and recycled Cu-Mn mixed oxides are shown in Fig. 1. We can see that the IR spectrums of fresh and recycled Cu-Mn mixed oxides look nearly the same, but there still exists differences among them. The broad and intense absorption peak at $3300-3500 \text{ cm}^{-1}$ considers being the stretching vibration of the internal hydroxyl groups for all samples. The broad absorption peak at 1500–1600 cm^{-1} corresponding to the bending vibration of the internal OH groups from water molecules are observed. It is apparent to recognize that the sharp and intense absorption peak at 1363 cm⁻¹ attributes to the bending vibration of the internal CO_3^{2-} for the samples of fresh and recycled Cu-Mn mixed oxides. The characteristic absorption peak of the stretching vibration and framework vibration of M-O-M can be found at $400-700 \text{ cm}^{-1}$. The IR spectra of fresh and recycled Cu-Mn mixed oxides, suggesting that Cu-Mn mixed oxides are of structural stability.

Powder X-ray diffraction

The XRD patterns of fresh, recycled Cu–Mn mixed oxides and various Cu–Mn oxides at different temperature are presented in Figs. 2 and 3. The data were treated with Jade (Version 6.0) software and

 Table 1
 The content of Cu–Mn Ox catalysts measured by ICP and BET methods

Sample	[Mn]/([Cu] + [Mn])		$S_{BET}/m^2 g^{-1}$	Pore volume/cm ³ g ⁻¹	Pore diameter/nm
	Initial solution	Solids material			
Fresh	0.40	0.41	59.69	0.45	27.86
Cu–Mn					
Recycle	_	0.39	33.38	0.23	28.21
Cu–Mn					



Fig. 1 The FT-IR spectra: a, fresh Cu–Mn Ox; b, c, d and e orderly from the second to the fifth, recycled Cu–Mn Ox

identification of the crystalline phases was made by comparison with the ICDD (2004) files. As it can be seen, there are a few differences in feature between

Fig. 2 The XRD patterns of Cu–Mn Ox: *filled square*, Cu_{1.5}Mn_{1.5}O₄; *filled circle*, CuO; *filled upright triangle*, Mn₃O₄; calcined temperature: *a* 378 K; *b* 573 K; *c* 673 K

XRD patterns of the single and mixed manganese and copper oxide catalysts for the diffraction peaks which were broad and weak, we were able to identify, including those with the spinel structure. The catalysts prepared from mixed solutions of manganese(II) and copper nitrate contained not only individual copper(II) and manganese(IV) oxides but also the mixed oxides Cu1.5Mn1.5O4, Cu1.4Mn1.6O4, CuMn2O4, and etc. Surprisingly, calcination at 573 K or higher temperatures, there was no substantive change in composition compared with the temperatures of 378 K, showing the catalyst has a good thermal stability. The results indicated that Cu-Mn mixed oxides may be responsible for recycled, at least, four times without loss of the activity (Fig. 3). The XRD data attributes to Cu-Mn due to the report of Ivanets [34], suggesting the formation of a well structural hopcalite (copper-manganese oxide).

Figs. 2 and 3. Though it was hard to distinguish the



Fig. 3 The XRD patterns of Cu–Mn Ox: *filled square*, Cu_{1.5}Mn_{1.5}O₄; *filled circle*, CuO; *filled upright triangle*, Mn₃O₄; *d*, fresh Cu–Mn Ox; *e*, *f*, and *g* orderly from the second to the fourth, recycled Cu–Mn Ox

Thermo gravimetry and differential thermal analyses

TG/DTA analysis of Cu–Mn Ox was measured by synchronous thermal analyzer to study the course of the thermal decomposition. The consequence of Cu–Mn Ox was exhibited as a mode sample in Fig. 4. As it can be seen, the curves of TG/DTA has two stages of weight over the temperature range of 423–573 and 573–873 K and the



Fig. 4 TG/DTA curves of Cu-Mn Ox

total weight loss was about 12 %. The weight loss in temperature range of 423–573 K accounts for about 8–9 %, which is attributed to the removal of internal and weakly adsorbed water molecules. The second weight loss accounts for 3–4 %, which is due to the decomposition of carbonate anions from the internal causing the break of the structure. The whole curve of DTA was shown that the material was exothermic except that at the temperature of 423–523 K which was endothermic.

Scanning electron microscope

The scanning electron micrographs (SEM) of fresh and recycled Cu–Mn Ox are displayed in Fig. 5. It is clear to see that the materials are made up of aggregate of regular morphology and the particle size is homogeneous and tiny; after the oxidation reaction, the particle size of Cu–Mn Ox slightly change and become uneven and loose.

Effect of calcined temperature on the reaction

The catalytic performances of different calcined temperature catalysts in the oxidation of isolongifolene by molecular oxygen and TBHP are compared in Table 2. We



100 mm EHT = 3.00 kV WD = 8.3 mm Mag = 50.00 K X Signal A = SE2 20 Nov 2015 GXUN

Fig. 5 The SEM micrographs: a, fresh Cu-Mn Ox; b, c, and d orderly from the second to the fourth, recycled Cu-Mn Ox

Calcined temp./K	Solvent	TBHP/mmol	Time/h	Conversion/%	Selectivity/%
378	CH ₃ CN	3	24	100	89.5
573	CH ₃ CN	3	24	100	93.4
673	CH ₃ CN	3	24	100	95.2

 Table 2
 The different calcined temperature catalysts oxidation of isolongifolene

All reactions were carried out using isolongifolene (1 mmol), Cu–Mn Ox (100 mg), TBHP (3 mmol), and 4 cm³ CH₃CN, purged with molecular oxygen, A.T, 24 h. Selectivity (%) = yield (%)/conversion (%), determined by GC and GC–MS

can find that the Cu–Mn Ox (673 K) exhibits a maximum conversion (100 %) and selectivity (95.2 %) to isolongifolenone, and then followed by Cu–Mn Ox (573 K) conversion (100 %) and selectivity (93.4 %). Cu–Mn Ox (378 K) shows an inferior selectivity (89.5 %). The results indicate that oxides calcined at a temperature of 673 K lead to formation of highly active species on the surface of Cu– Mn Ox for the oxidation, so we chose it as catalyst of all experiments we had done.

Effect of solvent on the reaction

The rates, equilibria, the selectivity and the products of chemical reactions can be strongly influenced by the solvent. Therefore, the effect of organic solvents on the oxidation of isolongifolene using Cu–Mn Ox catalysts was studied and the results were illustrated in Fig. 6. Among the solvents studied, acetonitrile shows excellent conversion (100 %) and selectivity (95.2 %) to isolongifolenone, and then followed by acetone (97.7 % conversion, 88.3 % selectivity), tetrahydrofuran (84.1 % conversion, 79.1 % selectivity), chloroform (79.2 % conversion, 66.8 % selectivity), dichloromethane (61.7 % conversion, 57.0 % selectivity), ethylacetate (45.4 % conversion, 54.8 % selectivity), acetic



Fig. 6 The influence of solvents on the reaction. Conditions: 1 mmol isolongifolene, 100 mg Cu–Mn Ox, 3 mmol TBHP, 4 cm³ solvent, and 1 atm O₂, A.T, 24 h. Selectivity (%) = ^a yield (%)/conversion (%), ^adetermined by GC

acid (44.5 % conversion, 47.2 % selectivity) and methanol (55.7 % conversion, 32.8 % selectivity). The results are conformed to the recent studies of the Cu-catalyzed allylic oxidation of alkenes performed in acetonitrile or acetone [35].

The blank experiment among catalyst, TBHP and O₂

As we known, these factors including Cu–Mn Ox, TBHP, and O_2 have much effect on the reaction. So, to clarify the relations, the blank experiments were carried out. From the Table 3, it can be seen clearly that both the conversion and the selectivity were poor when lack one of them. Therefore, to complete this reaction efficiently, Cu–Mn Ox, TBHP, and O_2 are indispensable.

Designs of experiments for isolongifolene to isolongifolenone

To seek for an optimal reaction condition, we design DoE experiments using statistical methods, which is a statistical approach that defines a domain for every variable involved in a reaction [36]. We investigated two variables, the equivalents of TBHP and the amount of Cu–Mn Ox. We adopted a 3^2 full factorial design to carry out 11 experiments (Table 4). The curved shape of the obtained response surface (Fig. 8) showed that higher amounts of Cu–Mn Ox and TBHP would not proceed in significant higher yields for the allylic oxidation. The vertical line in

Table 3 The blank experiment among catalyst, TBHP, and O_2 on isolongifolene to isolongifolenone (the "+" or "-" stands for add or none)

Entry	Cu–Mn Ox	TBHP	O ₂	Conversion/%	Selectivity/%
1	+	+	_	44.7	39.9
2	+	_	+	27.6	34.0
3	-	+	+	39.5	37.3
4	+	+	+	100	95.2

Conditions: isolongifolene (1 mmol), TBHP (3 mmol), Cu–Mn Ox (100 mg), O₂ (1 atm), and 4 cm³ CH₃CN, A.T, 24 h. Selectivity (%) = yield (%)/conversion (%), determined by GC

 Table 4 Factors and levels of three full factorial design for isolongifolenone

Factor	High level	Low level	Units
Cu–Mn Ox	150	50	mg
TBHP	5	0.5	equiv

the Pareto plot (Fig. 7) indicates a level of 95 % confidence, representing the TBHP has a great influence on the reaction. The statistical analysis of the model obtained (Tables 4, 5) displayed that the main factor involved was the amount of TBHP employed in the reaction. The response surface is displayed in Fig. 8. The excellent result attributes to 100 mg/mmol Cu–Mn Ox and 3 equiv TBHP, which led to 95.2 % yield of isolongifolenone analyzed by GC.

Reused of catalyst

To evaluate the reusability of Cu–Mn mixed oxide catalyst, a recycling test was carried out using the recovered catalysts for oxidation isolongifolene (Table 6). The reaction was carried



Fig. 7 Pareto plot for the oxidation of isolongifolene

Table 5 Three-level full factorial design for isolongifolenone 1a

Cu_Mn Ox/mg	TBHP/equiv	Vield ^a /%
Cu–ivili Ox/ilig	I BIII /equiv	1 ieiu / //
100	3	95.2
100	5	93.4
100	3	95.1
150	1	55.4
150	3	93.0
50	3	76.3
50	5	60.1
50	1	38.1
100	1	54.7
100	3	94.9
150	5	89.4
	Cu–Mn Ox/mg 100 100 100 150 150 50 50 50 50 100 10	Cu–Mn Ox/mg TBHP/equiv 100 3 100 5 100 3 150 1 150 3 50 3 50 5 50 1 100 1 100 1 100 5

All reactions were carried out using isolongifolene (1 mmol), TBHP, Cu–Mn Ox, 4 cm³ CH₃CN, and O₂ (1 atm), A.T, 24 h

^a Determined by GC



Fig. 8 Response surface for the synthesis of isolongifolenone (1a)

Table 6 Reused of catalyst

Cycles (n)	Conversion/%	Selectivity/%
1	100	95.2
2	100	91.1
3	100	89.3
4	100	87.0

Conditions: 1 mmol isolongifolene, 100 mg catalysts, 3.0 mmol TBHP, and 4 cm³ CH₃CN, purged with molecular oxygen, A.T, 24 h. Selectivity (%) = yield (%)/conversion (%), determined by GC

out with molecular oxygen and TBHP as the oxidant under ambient temperature. Upon completion of the reaction, products were extracted with dichloromethane and the yields were determined by GC. The resulting Cu–Mn Ox catalyst with 96.5 % yield was collected and activated in the oven at 378 K for 10 h. The recycled experiment was carried out with 100 mg recycled Cu–Mn Ox under the same condition. As can be seen from Table 6, the Cu–Mn Ox catalyst could be used four times with no significant decrease in the yields. Consistent with these results, no apparent changes could be discovered between the FT-IR spectra and XRD patterns of the fresh and recycled catalysts. Those mean Cu–Mn mixed oxide was a stable, heterogeneous catalyst for allylic oxidation.

Oxidation of different cyclic olefins catalyzed by Cu-Mn Ox

To further probe the generality of this catalytic system, various cyclic olefins were investigated under the optimal condition and the results are summarized in Table 7. Cyclohexene was oxidized with 100 % conversion and 93.9 % selectivity for 2-cyclohexene-1-one (**1b**). Interestingly, 2-cyclohexene-1-one undergoes epoxidation with 100 % conversion and 92.8 % selectivity for 7-oxabicy-clo[4.1.0]heptan-2-one (**2a**) and no cyclohex-2-ene-1,4-dione. Meanwhile, when indane was oxidized, 93.1 % conversion 81.6 % selectivity for 1-indanone (**3a**) was obtained. When oxidation of α -pinene and β -pinene was performed, 85.2 % conversion was obtain with 85.1 %

Table 7 Results of oxidation ofcyclic olefins over Cu–Mn Ox

Entry	Substrate	Product	Conversion / %	Selectivity / %
1		1 b	100	93.9
2		0 0 2a	100	92.8
3		Jaa Jaa	93.1	81.6
4		4a	85.2	85.1
5		0 5a	90.2	98.5
6		6a HO	87.8	89.2
		-		

All reactions were done using alkene (1.0 mmol), Cu–Mn Ox (100 mg), TBHP (3 mmol), 4 cm³ CH₃CN, and O₂ (1 atm), A.T, 24 h. Selectivity (%) = yield (%)/conversion (%), determined by GC

selectivity of 4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-one (**4a**) and 90.2 % conversion was afforded 98.5 % selectivity of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (**5a**), respectively. Surprisingly, when terpinolene was oxidized, only gave corresponding rearrangement product, 87.8 % conversion and 89.2 % selectivity for 2-(4-methyl-phenyl)propan-2-ol (**6a**) was obtained.

Conclusion

In using a catalytic amount of mixed copper-manganese oxide, the allylic oxidation of cycloolefins in the presence of 1 atm O_2 and TBHP has been efficiently carried out in

good yields without using excesses of the alkene. Furthermore, DoE was designed to confirm the best conditions of allylic oxidation. Besides, the catalyst was identified to be stable and reusable without substantial loss of activity.

Experimental

All the reagents in the experiment were of analytical grade except industrial grade isolongifolene, terpinolene, and molecular oxygen, which were used without further disposal, if not mentioned. Deionized water was used throughout this experiment. Each of reaction was performed with magnetic stirrers under an ambient temperature. ICP were measured with Optima 5300 DV, FT-IR spectra were determined on a MAGNA-1R550 using KBr discs in the 400–4000 cm^{-1} region under atmospheric conditions. The specific surface areas were determined using the BET equation and the microspore volumes by the de Boer's t-method on ASAP2020M. Powder XRD were performed on a XD-3 diffractometer with CuKa radiation $(\lambda = 1.5406 \text{ nm})$ scanning from 10 to 70° (20) at a scan rate of 0.5 min^{-1} and using silicon as an external standard. The working voltage and the current were 36 kV and 25 mA. TG/DTA measurements of the samples were measured with STA instruments STA449 F3 Jupiter thermal analyzer used α -Al₂O₃ crucible in the temperature range of 303–1173 K at a heating rate of 283 K min⁻¹ under nitrogen conditions. SEM images were obtained with a SUPRA 55 Sapphire microscope operating at acceleration voltages 10 kV, and magnification values up to 50 KX. The reaction products of oxidation were analyzed using GC-7890A gas chromatograph with a HP-5 column $(30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m})$ in flame ionization detector (FID) and were confirmed by gas chromatograph-mass spectra (GC-MS) on Perkin Elmer Instruments (Clarus500) with ionization energy of 70 eV. ¹H NMR spectra were recorded on 600 MHz NMR spectrometer (Bruker AV600), using tetramethylsilane (TMS) as the internal standard and CDCl₃ as the solvent. X-ray single crystal diffraction experiments were carried out on with MoKa radiation ($\lambda = 0.71073$ Å) using a bruker SMART APEX CCD diffractometer at 296 K.

Catalyst preparation

Catalyst was prepared by co-precipitation method based on the paper which was reported by Jonesa C [29]. An alkaline solution containing 1270 mg Na₂CO₃ (12 mmol) and 5200 mg NaOH (130 mmol) in 100 cm³ deionized water was added dropwise over 1.5 h to another solution containing Cu (NO₃)₂·3H₂O and 50 % Mn(NO₃)₂ aquatic solution in 50 cm³ deionized water. The molar ratio [Mn]/ ([Cu] + [Mn]) is 0.40. The suspension solution was then stirred at 343 K for 22 h, and was gradually changed in color from blue to black during the course of reaction. The black precipitate was filtered and the residue was washed with warm deionized water. The solid was then dried in the oven at 378 K for 10 h and then calcined in muffle furnace at different temperature 573 or 673 K for 10 h. In the finial, it was left exposed to air 3 days before use.

General procedure for the allylic oxidation

Alkene (1 mmol), Cu–Mn Ox (100 mg), and amount of TBHP were stirred in 4 cm^3 of acetonitrile in a 50 cm³ round-bottom flask equipped with a magnetic stirrer.

Initially, stir vigorously for 30 min to form a subtly dispersed heterogeneous system. 70 % aqueous solution of TBHP was added to the system and then purged with oxygen. The reaction mixture was stirred for the required time (about 20-24 h). Reactions were measured by gas chromatography (GC) using naphthaline as an internal standard. To take the small portion for the GC analysis at appropriate time intervals, the small portions were diluted 20-fold with CH₃CN before the analysis. Saturated aqueous $Na_2S_2O_3$ solution (10 cm³) was added to remove any redundant TBHP after filtered out the residue, and the solution was extracted with dichloromethane $(3 \times 50 \text{ cm}^3)$, washed with 10 cm³ saturated aqueous EDTA solution, and dried over anhydrous Na₂SO₄. The solvent was then evaporated to dryness. The resulting oily residue was purified by silica gel column chromatography (petroleum ether/EtoAc = 20:1) and analyzed by ¹H NMR, X-ray single crystal diffraction, or GC and GC-MS.

The recovery of this black powder by filtration, drying and its submission to X-ray diffraction analysis, allowed us to know that catalytic capacity of Cu–Mn Ox whether there is a change or not after the reaction. The recycling experiments were carried out as follows: After the completion, the catalyst was filtered out and washed with warm water for more than three times. Then, it was activated by dryness in the oven at 378 K for 10 h. The structures of the products were confirmed by GC–MS (Perkin Elmer Instruments Clarus500, 70 eV) by comparison with authentic samples. Product isolongifolenone (GC yield 95.2 %) was isolated by column chromatography (silica) using mixtures of petroleum ether and EtOAc (20:1) as eluents (isolated yield 82.6 %) and identified by ¹H NMR, IR, and X-ray crystal diffraction (Fig. 9).



Fig. 9 ORTEP view of isolongifolenone

CCDC 1440043 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallo-graphic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or e-mail:deposit@ccdc.cam.ac.uk.

Acknowledgments We are Grateful to colleges and universities in Guangxi Science and Technology Research projects (ZD2014046, YB2014331), Natural Science Foundation of Guangxi Zhuang Autonomous Region (No. 2014GXNSFAA118032) and Graduate education innovation project of Guangxi University for nationalities (gxun-chxs2015087) for financial support.

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