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Selective oxidation of benzylic alcohols using

copper-manganese mixed oxide nanoparticles

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#### **KEYWORDS**

Copper-manganese oxide; Catalyst; Oxidation; Benzylic alcohols **Abstract** The catalytic activity of copper-manganese (CuMn<sub>2</sub>) mixed oxide nanoparticles (Cu/Mn = 1:2) has been studied for the selective oxidation of benzylic alcohols to the corresponding aldehydes using molecular oxygen as an oxidizing agent. The CuMn<sub>2</sub> mixed oxide showed excellent catalytic activity for the oxidation of benzylic alcohols to the corresponding aldehydes with high selectivity (>99%). The complete conversion (100%) of all the benzylic alcohols to the corresponding aldehydes is achieved within a short reaction period at 102 °C. The catalytic performance is obtained to be dependent on the electronic and steric effects of the substituents present on the phenyl ring. Electron withdrawing and bulky groups attached to the phenyl ring required longer reaction time for a complete conversion of the benzylic alcohols.

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## 1. Introduction

Research on the catalytic oxidation of benzylic alcohols to the corresponding aldehydes has been a subject of great interest as the products are important precursors to pharmaceuticals and fine organics (Köchritz et al., 2006; Enache et al., 2006; Beller and Bolm, 2004). The selective catalytic oxidation of alcohols

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to the corresponding aldehydes is of significant importance in view point of laboratory synthesis and industrial manufacturing (Lenoir, 2006; Tojo and Fernandez, 2006; Matsumoto et al., 2008; Fan et al., 2009). Metal-catalyst reactions for the selective oxidation of alcohols to the corresponding aldehydes with inexpensive oxidants, such as molecular oxygen have been recognized as environmentally benign methods in synthetic chemistry and have attracted great attention from both economic and environmental point of view (Pillai and Demessie, 2004; Zhan and Thompson, 2004; Mallat and Baiker, 2004). Although many studies have been reported using transition metal containing catalysts, disadvantages of the catalysts are, use of expensive noble metals as supports/influence or difficultly in preparation. Therefore, use of various abundant

1878-5352 © 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. http://dx.doi.org/10.1016/j.arabjc.2013.05.012 and cheap transition metals, like Cu- and Mn-containing compound as catalysts for the oxidation of benzylic alcohols to the corresponding aldehydes is still in demand.

Numerous studies have also been devoted to non-noble metals or metal-based catalysts, such as Cu (Perez et al., 2012), Ni (Ali et al., 2011a), Fe (Naik et al., 2011), V (Behera and Parida, 2012), Co (Seyedi et al., 2010), Ag (Deng et al., 2010), Cr (Ozturk et al., 2008), Mo (Rao et al., 2011), Zn (Ali et al., 2009) and Re (Paraskevopoulou et al., 2005) for oxidation of benzyl alcohol with molecular oxygen. Among the various abundant and cheap transition metals, Cu and Mncontaining compound as catalysts is continuing to inspire research for developing a newer and green method for the selective oxidation of benzylic alcohols with molecular oxygen. There are some reports on Mn-containing catalysts for oxidation of benzylic alcohols using molecular oxygen, but those involved supports or ligands such as octahedral molecular sieves (Suib, 2008; Schurz et al., 2009; Son et al., 2001), various kinds of alumina as support (Tang et al., 2009a, b, c, 2010; Yang et al., 2008), supported on cerium (IV) (Sato and Komanova 2009), combination with TEMPO (2.2.6.6-tetramethyl-piperidyl-1-oxyl) (Yang et al., 2008 and Guo et al., 2007). Mn(II) complexes (Mahdavi et al., 2008) immobilized in the pore channels of mesoporous hexagonal molecular sieves and hexadentate Q<sub>3</sub>Mn<sup>III</sup> complexes (Ye et al., 2009) have been reported for oxidation of alcohols using TBHP and H<sub>2</sub>O<sub>2</sub> as oxidant, respectively. An octahedral molecular sieve, a synthetic manganese oxide with a tunnel structure, was reported as a superior catalyst for the aerobic oxidation of alcohols in liquid-phase in the presence of molecular oxygen (Suib 2008). We have reported (Ali et al., 2011b) CuMn<sub>4</sub> (Cu/ Mn = 1:4) mixed oxide for the oxidation of benzyl alcohol to benzaldehyde with molecular oxygen without use of any support.

In our previous study (Ali et al., 2013a) we have shown that copper-manganese CuMn<sub>2</sub> mixed oxide (Cu/Mn = 1:2) catalyst was very effective for oxidation of benzyl alcohol. Herein, we report an evaluation of the same catalyst (CuMn<sub>2</sub> mixed oxide nanoparticles with Cu/Mn = 1:2) for the selective oxidation of benzylic alcohols to the corresponding aldehydes with molecular oxygen. The effect of the catalytic activity on the para-benzylic alcohols substituted with  $-CH_3$ ,  $-OCH_3$ ,  $-NO_2$ , -Cl,  $-C(CH_3)_3$ ,  $-CF_3$  groups and meta-benzylic alcohol substituted with  $-NO_2$  group has been compared. The catalytic activity of the CuMn<sub>2</sub> oxide was also tested for citronellol.

## 2. Experimental

### 2.1. Catalyst preparation

The CuMn<sub>2</sub> mixed oxide (Cu/Mn = 1:2) nanoparticles were prepared by co-precipitation method using the required amount of precursors Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub> as described in our earlier paper (Ali et al., 2013a). All reagents used were of analytical grade and purchased from MERCK and BDH Chemical Ltd., and used without further purification. The powdered catalyst was calcined at 300 °C in air for 12 h before using it for oxidation reaction. The catalyst was prepared with the nominal composition of CuMn<sub>2</sub>O<sub>4</sub>, while the final composition was obtained to be CuMn<sub>1.87</sub>O<sub>4.07</sub> according to the chemical analyses. Benzyl alcohol and its derivatives (para-benzylic alcohols substituted with  $-CH_3$ ,  $-OCH_3$ ,  $-NO_2$ , -Cl,  $-C(CH_3)_3$ ,  $-CF_3$  groups and meta-benzylic alcohol substituted with  $-NO_2$  group) were obtained from Aldrich Chemical Ltd. and citronellol was obtained from Merck Chemical Ltd. All these chemicals were utilized as received without further purification. The detailed characterization of the catalyst was described in our previous work (Ali et al., 2013a).

#### 2.2. Oxidation reaction and product analysis

The CuMn<sub>2</sub> mixed oxide nanoparticles were tested for the catalvtic activity of benzyl alcohol and its derivatives (para-benzylic alcohols substituted with -CH<sub>3</sub>, -OCH<sub>3</sub>, -NO<sub>2</sub>, -Cl, -C(CH<sub>3</sub>)<sub>3</sub>, -CF<sub>3</sub> groups and meta-benzylic alcohol substituted with -NO<sub>2</sub> group) and citronellol in liquid phase oxidation using molecular oxygen. The reactions were carried out in a three-necked flask connected with oxygen gas cylinder and condenser under atmospheric pressure. In a typical catalytic experiment, 200 mg catalyst and 2 mmol substrates were charged in 10 mL toluene (free from sulfur, min. assay 98%, WINLAB LIMITED, UK) as solvent. The mixture was then heated on an oil bath at 100 °C. Oxygen was bubbled at a flow rate of 20 mL min<sup>-1</sup> into the mixture with continuous stirring using a magnetic bar. The reaction temperature was maintained at 100-102 °C. A small amount of reaction mixture was collected after a certain time. The collected reaction mixtures were separated by centrifugation and the liquids were analyzed by gas chromatography (GC) on GC-7890A Agilent Technologies Inc. equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column. The conversions of the alcohols and the selectivity to the corresponding aldehydes were calculated by the peak areas.

#### 3. Results and discussion

In our previous study (Ali et al., 2013a), the amount and precalcination temperature of CuMn<sub>2</sub> mixed oxide nanoparticles catalyst were optimized to be 200 mg and 300 °C, respectively for the selective oxidation of alcohol using molecular oxygen. To evaluate the scope of the CuMn<sub>2</sub> mixed oxide as catalyst, oxidation reactions with various electron withdrawing and electron donating substituents on benzyl alcohol were carried out under the same conditions used for the benzyl alcohol (Ali et al., 2013a). A complete conversion (100%) of the benzylic alcohols to the corresponding aldehydes was obtained within short reaction time at 102 °C. The selectivity of the oxidation of benzylic alcohols to the corresponding aldehydes was obtained to be >99% for all the reactions. The oxidation reaction for citronellol was also carried out over the CuMn2 mixed oxide under the same conditions and obtained only 6.22% conversion with specific activity of  $0.16 \text{ mmol g}^{-1}\text{h}^{-1}$  after 4 h while the selectivity was >99%. It should be noted that, under the same reaction conditions no detectable conversion of benzylic alcohols was obtained in the absence of catalyst, also only solvent toluene (without alcohols) showed no formation of aldehyde in the presence of the catalyst.

Table 1 shows conversion, specific activity and selectivity of the benzyl alcohol and its derivatives as a function of time. It can be seen that the complete conversion of the benzylic alcohols to the corresponding aldehydes is achieved at different

Entry	Substrate	Time (min)	Product	Conversion (%)	Selectivity (%)	Specific activity (mmol $g^{-1} h^{-1}$ )
1	ОН	20	0 H	100	> 99	30
2	CH <sub>3</sub>	20	O H CH <sub>3</sub>	100	> 99	30
3	OH OCH <sub>3</sub>	20	O H OCH3	100	>99	30
4	OH NO <sub>2</sub>	25	O H NO <sub>2</sub>	100	> 99	24
5	OH CI	50	O CI	100	> 99	12
6	OH	30	°→H ↓	100	>99	20
7	F F F	60		100	> 99	10

Table 1Selective oxidation of benzyl alcohols into corresponding aldehydes over  $CuMn_2$  mixed oxide nanoparticles catalyst usingmolecular oxygen as oxidant.

reaction times, but the selectivity to the corresponding aldehydes remained unchanged (>99%) for all the reactions. The catalytic activity of CuMn<sub>2</sub> mixed oxide nanoparticles is very low for the oxidation of citronellol into citronellal. Only a 6.22% conversion to citronellal is obtained catalyzed by CuMn<sub>2</sub> mixed oxide after 4 h. This low conversion is probably

due to the absence of conjugated system (like benzene ring) in the  $\beta$ -position of the OH goup.

The complete conversion of substituted benzyl alcohols with electron donating  $-CH_3$  and  $-OCH_3$  groups attached to the para-position of the phenyl ring is obtained after 20 min. with specific activity 30 mmol g<sup>-1</sup>h<sup>-1</sup>, which is equal to that



Reaction conditions: 200 mg catalyst, 2 mmol benzyl alcohol in 10 mL toluene, reaction temperature 102 °C.

of benzyl alcohol (Table 1). May be the electron donating groups -CH<sub>3</sub> and -OCH<sub>3</sub> have very little effect which could not be detected within the present time interval (5 min). We obtained little effect of these groups in the oxidation reactions over CuMn (Cu/Mn = 1:1) mixed oxide in our earlier work (Ali et al., 2013b). Attachment of electron withdrawing groups (-NO<sub>2</sub>, -Cl) to the para-position of the phenyl ring decreased the efficiency of the oxidation reaction and required a longer time for a complete conversion compared with that of the benzyl alcohol. The results indicated that electron density on the phenyl ring played an important role in the reactivity of the oxidation reaction. The complete conversion of alcohols with electron withdrawing groups -NO2 and -Cl on the para-position of the phenyl ring was observed after 25 and 50 min, respectively. -NO<sub>2</sub> is stronger electron withdrawing group compared to -Cl, but it is not clear why -Cl decreased reactivity more than that of -NO<sub>2</sub> group. The stronger electron withdrawing nature of -NO2 group is mainly due to resonance effect rather than inductive effect (I). -Cl has a higher negative inductive effect (-I) than that of -NO2, which may be the reason that attachment of the -Cl to the benzene ring deactivating the oxidation reaction more than that of the -NO<sub>2</sub> group. p-Nitro benzyl alcohol oxidized in 25 min. whereas it took 100 min. for the oxidation of m-nitro benzyl alcohol. Thus, substituent (-NO<sub>2</sub>) attached to the meta-position of the phenyl ring affects more than that of para-position. Steric hindrance is another important factor that affects the reactivity as bulky electron donating  $-C(CH_3)_3$  and electron withdrawing  $-CF_3$ groups attached to the phenyl ring decreased the efficiency of the reaction. Therefore, it can be concluded that oxidation reaction of benzylic alcohols catalyzed by CuMn<sub>2</sub> mixed oxide is influenced by both electronic and steric effects.

The morphology of the catalysts was studied with a combination of various characterization techniques, which is described in detail in our earlier work (Ali et al., 2013a). The CuMn<sub>2</sub> mixed oxide catalyst pre-calcined at 300 °C was found to be a mixture of three phases, cubic CuMn<sub>2</sub>O<sub>4</sub> (ICSD #93434), hexagonal MnO<sub>2</sub> (ICSD #76430) and monoclinic CuO (ICSD #92368) as was indicated in X-ray diffraction pattern (Fig. 1). Peaks of the corresponding phases are indicated



**Figure 1** Powder X-ray diffraction pattern of  $CuMn_2$  mixed oxide pre-calcined at 300 °C. Symbols  $\blacklozenge$ ,  $\diamondsuit$  and  $\blacklozenge$  indicate hexagonal MnO<sub>2</sub>, monoclinic CuO and cubic CuMn<sub>2</sub>O<sub>4</sub> phases, respectively.

by different symbols in Fig. 1. The average crystallite size of the catalyst was determined to be 29.26 nm from XRD linebroadening (determined by the Scherrer equation) using peaks appeared at 35.62, 37.40, 38.88, 42.47 and 48.69 in  $2\theta$  (Fig. 1).

TEM image of the catalyst (Fig. 2) shows that the existing phases are distributed over all the area and are not well crystalline. It appears as irregular-shaped agglomerates of major CuO and MnO<sub>2</sub> phases as observed in the X-ray diffraction pattern. The agglomerated particle morphology of the particle size was calculated using ImageJ 1.44 (Rasband, 2011) from the TEM image (Fig. 2). The mean particle size is obtained to be  $28.34 \pm 0.07$  nm (inset graph of Fig. 2), which is in good agreement with the crystallite size determined by the Scherrer equation using XRD line-broadening (29.26 nm).

The higher catalytic activity of the  $CuMn_2$  mixed oxide catalyst for oxidation of benzylic alcohols to the corresponding aldehydes may be attributed to the formation of amorphous



Figure 2 Transmission electron microscopy (TEM) image of  $CuMn_2$  mixed oxide pre-calcined at 300 °C. Particle size distribution determined from the TEM image is shown in graph (inset figure).

 $MnO_2$  and/or small crystallite size of the mixed oxide. This result is in agreement with the catalytic activity for oxidation of benzyl alcohol. The manganese oxide,  $MnO_2$  was reported as a highly active phase (Yang et al., 2007) and when it co-existed in CuMn<sub>2</sub> oxide showed a higher catalytic activity than that of pure  $MnO_2$  (Ali et al., 2013a) for oxidation of benzyl alcohol.

#### 4. Conclusions

The catalytic activity of CuMn2 mixed oxide nanoparticles catalyst for the oxidation of benzyl alcohol derivatives substituted with various electron donating  $(-CH_3, -OCH_3, -C(CH_3)_3)$  and electron withdrawing (-Cl, -NO<sub>2</sub>, -CF<sub>3</sub>) groups on the phenyl ring has been examined. The oxidation reactions of the benzylic alcohols were observed to proceed on the CuMn2 mixed oxide catalyst with high efficiency. The selectivity toward the corresponding aldehyde is obtained to be very high (>99%)for all the alcohols tested in this work. The oxidation reaction of citronellol provided only 6.22% conversion after 4 h while the selectivity >99% under the same condition. The selectivity remained unchanged for all the reactions although the conversions were found to be affected by the substituent groups. Alcohols having electron withdrawing and/or bulky groups required a longer reaction time compared with those having electron donating groups on the phenyl rings.

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### References

- Ali, S.R., Bansal, V.K., Khan, A.A., Jain, S.K., Ansari, M.A., 2009. J. Mol. Catal. A 303, 60–64.
- Ali, R., Siddiqui, M.R., Warthan, A.A., 2011b. Oxidation Commun. 34, 778–787.
- Ali, S.R., Chandra, P., Latwal, M., Jain, S.K., Bansal, V.K., Singh, S.P., 2011a. Chin. J. Catal. 32, 1844–1849.
- Ali, R., Adil, S.F., Al-warthan, A., Siddiqui, M.R.H., 2013a. J. Chem., dx.doi.org/10.1155/2013/367261.
- Ali, R., Assal, M.E., Al-warthan, A., Siddiqui, M.R.H., 2013b. Asian J. Chem. 25 (9), 4815–4819.
- Behera, G.C., Parida, K.M., 2012. Appl. Catal. A 413-414, 245-253.
- Beller, M., Bolm, C., 2004. Transition Metals for Organic Synthesis, 2nd ed. Verlag Gmbh & Co. KGaA, Weinheim, Germany.
- Deng, M., Zhao, G., Xue, Q., Chen, L., Lu, Y., 2010. Appl. Catal. B 99, 222–228.
- Enache, D.I., Edwards, J.K., London, P., Solsona-Espriu, B., Carley, A.F., Herzing, A.A., Watanabe, M., Kiely, C.J., Knight, D.W., Hutchings, G.J., 2006. Science 311, 362–365.
- Fan, J., Dai, Y., Li, Y., Zheng, N., Guo, J., Yan, X., Stucky, G.D., 2009. J. Am. Chem. Soc. 131, 15568–15569.
- Guo, Y., Zhao, J., Xu, J., Wang, W., Tan, F., Yang, G., Song, M.J., 2007. Nat. Gas Chem. 16, 210–212.
- Köchritz, A., Sebek, M., Dittmar, A., Radnik, J., Brückner, A., Bentrup, U., Pohl, M.-M., Hugl, H., Mägerlein, W., 2006. J. Mol. Catal. A: Chem. 246, 85–99.
- Lenoir, D., 2006. Angew. Chem. Int. Ed. 45, 3206-3210.
- Mahdavi, V., Mardani, M., Malekhosseini, M., 2008. Catal. Commun. 9, 2201–2204.
- Mallat, T., Baiker, A., 2004. Chem. Rev. 104, 3037-3058.
- Matsumoto, T., Ueno, M., Wang, N., Kobayashi, S., 2008. Chem. Asian J. 3, 196–214.
- Naik, R., Nizam, A., Siddekha, A., Pash, M.A., 2011. Ultrason. Sonochem. 18, 1124–1127.
- Ozturk, O.F., Karan, B.Z., Karabulut, S., 2008. Catal. Commun. 9, 1644–1648.

- Paraskevopoulou, P., Psaroudakis, N., Koinis, S., Stavropoulos, P., Mertis, K., 2005. J. Mol. Catal. A: Chem. 240, 27–32.
- Perez, Y., Ballesteros, R., Fajardo, M., Sierra, I., Hierro, I.D., 2012. J. Mol. Catal. A: Chem. 352, 45–56.
- Pillai, U.R., Demessie, E.S., 2004. Green Chem. 6, 161-165.
- Rao, P.S.N., Rao, K.T.V., Saiprasad, P.S., Lingaiah, N., 2011. Chin. J. Catal. 32, 1719–1726.
- Rasband W., 2011. ImageJ 1.440, National Institutes of Health, Bethesda, Maryland, USA. <a href="http://imagej.nih.gov/ij/">http://imagej.nih.gov/ij/</a> .
- Sato, T., Komanoya, T., 2009. Catal. Commun. 10, 1095–1098.
- Schurz, F., Bauchert, J.M., Merker, T., Schleid, T., Hasse, H., Glaser, R., 2009. Appl. Catal. A 355, 42–49.
- Seyedi, S.M., Sandaroos, R., Zohuri, G.H., 2010. Chin. Chem. Lett. 21, 1303–1306.
- Son, Y.C., Makwana, V.D., Howell, A.R., Suib, S.L., 2001. Angew. Chem. Int. Ed. 40, 4280–4283.
- Suib, S.L., 2008. Acc. Chem. Res. 41, 479-487.
- Tang, Q., Gong, X., Wu, C., Chen, Y., Borgna, A., Yang, Y., 2009a. Catal. Commun. 10, 1122–1126.

- Tang, Q., Huang, X., Chen, Y., Liu, T., Yang, Y., 2009b. J. Mol. Catal. A: Chem. 301, 24–30.
- Tang, Q., Huang, X., Wu, C., Zhao, P., Chen, Y., Yang, Y., 2009c. J. Mol. Catal. A: Chem. 306, 48–53.
- Tang, Q., Gong, X., Zhao, P., Chen, Y., Yang, Y., 2010. Appl. Catal. A 389, 101–107.
- Tojo, G., Fernandez, M., 2006. In: Tojo, G. (Ed.), Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice. Springer, New York.
- Yang, S., Wang, L., Liu, Y., Cao, Y., He, Y., Fan, K.N., 2007. Catal. Commun. 8 (12), 2181–2185.
- Yang, G., Zhu, W., Zhang, P., Xue, H., Wang, W., Tian, J., Song, M., 2008. Adv. Synth. Catal. 350, 542–546.
- Ye, Z., Fu, Z., Zhong, S., Xie, F., Zhou, X., Liu, F., Yin, D., 2009. J. Catal. 261, 110–115.
- Zhan, B.Z., Thompson, A., 2004. Tetrahedron 60, 2917-2935.