

Research Article

Identification of Active Phase for Selective Oxidation of Benzyl Alcohol with Molecular Oxygen Catalyzed by Copper-Manganese Oxide Nanoparticles

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Catalytic activity of copper-manganese mixed oxide nanoparticles ($\text{Cu/Mn} = 1:2$) prepared by coprecipitation method has been studied for selective oxidation of benzyl alcohol using molecular oxygen as an oxidizing agent. The copper-manganese (CuMn_2) oxide catalyst exhibited high specific activity of $15.04 \text{ mmol g}^{-1} \text{ h}^{-1}$ in oxidation of benzyl alcohol in toluene as solvent. A 100% conversion of the benzyl alcohol was achieved with >99% selectivity to benzaldehyde within a short reaction period at 102°C . It was found that the catalytic performance is dependent on calcination temperature, and best activity was obtained for the catalyst calcined at 300°C . The high catalytic performance of the catalyst can be attributed to the formation of active MnO_2 phase or absence of less active Mn_2O_3 phase in the mixed CuMn_2 oxide. The catalyst has been characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer Emmett-Teller (BET) surface area measurement, and Fourier transform infrared (FT-IR) spectroscopies.

1. Introduction

Selective oxidation of alcohols to the corresponding aldehyde has been a subject of intense research as these transformations have a significant impact for laboratory synthesis and industrial manufacturing [1–4]. In particular, benzaldehyde is the most desirable as important precursor and intermediates in pharmaceutical and fine organics [5, 6]. With the increasing environmental concerns, selective oxidation of alcohols to the corresponding aldehydes with environmentally benign inexpensive oxidants, such as molecular oxygen, have attracted great attention from both economic and environmental points of view [7–10]. Many studies have been reported on oxidation of benzyl alcohol to benzaldehyde with molecular oxygen where addition of supports and promoters, visible light irradiation, and process in combination with TEMPO/PINO have been used to improve the catalytic systems [10–17]. A significant number of studies on catalytic oxidation using precious metal or metal-based compounds as catalysts, such as Au [18, 19], Pd [20, 21], Ru [22, 23], and Pt [24, 25], have been reported for selective oxidation of benzyl

alcohol. These catalysts suffer from high cost and limited availability. Therefore, it is highly desirable to investigate and develop inexpensive catalysts consisting of two 3d transition metals because these metals offer environmentally benign and cost-effective alternative to noble metal catalysts.

Whilst numerous studies have been devoted to nonnoble metals or metal-based catalysts, such as Cu [26], Ni [27], Fe [28], V [29], Co [30], Ag [31], Cr [32], Mo [33], Zn [34], and Re [35] for oxidation of benzyl alcohol with molecular oxygen, there is renewed interest for searching new transition-metal catalyst with molecular oxygen. Among a series of mixed transition metals, Mn- and Cu-containing mixed layered double hydroxide [36] and hydrotalcite-like solid [37] exhibited high catalytic activity for oxidation of benzyl alcohol to benzaldehyde. As a consequence, use of various abundant and cheap transition metals like Cu and Mn-containing compound as catalysts is continuing to inspire research for developing newer and green method for selective oxidation of benzyl alcohol with molecular oxygen.

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 [38]. Catalytic properties of manganese-based octahedral molecular sieves of type K-OMS-2 were studied by Fanny Schurz et al. [39, 40] for oxidation of benzyl alcohol with molecular oxygen and reported that the catalyst is superior in activity to that of crystalline β - MnO_2 and inferior to that of amorphous MnO_2 . Manganese oxides MnO_x calcined at different temperatures from 110° to 600°C exhibited 100% selectivity for oxidation of benzyl alcohol to benzaldehyde [41]. The amorphous manganese oxide MnO_{x-110} possesses higher surface area as well as catalytic activity than those MnO_x -(200–600). Under controlled microwave irradiation, manganese oxide α - MnO_2 has been reported [42] to be highly selective catalyst in liquid-phase solvent-free oxidation for the oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. Alumina-supported K-Mn mixed oxide [43] showed enhanced catalytic performance for selective oxidation of benzyl alcohol with molecular oxygen. The enhancement of the activity was attributed to the formation of α - MnO_2 rather than β - MnO_2 on coimpregnation of potassium to the $\text{Mn}/\gamma\text{-Al}_2\text{O}_3$. Highly dispersed manganese oxides supported on activated carbon (Mn/AC) [44] and alumina ($\text{Mn}/\gamma\text{-Al}_2\text{O}_3$) [45] showed high efficiency for the aerobic oxidation of benzyl alcohol using molecular oxygen. Mn (II) complexes [46] immobilized in the pore channels of mesoporous hexagonal molecular sieves were obtained to be active in catalyzing the oxidation of benzyl alcohols with good conversion percentage and 100% selectivity using TBHP as the oxidant. $\text{Ru}/\text{MnO}_x/\text{CeO}_2$ [47] has been reported to have high catalytic activities for oxidation of benzyl alcohols at low temperature (27°C). Ye et al. [48] developed hexadentate $\text{Q}_3\text{Mn}^{\text{III}}$ complexes as efficient catalyst for oxidation of alcohols to the corresponding carbonyl compound using H_2O_2 .

Mn–Ni mixed hydroxide [49] catalyst was found to be efficient in aerobic oxidation of benzyl alcohol with molecular oxygen, where the highest conversion was achieved over Mn/Ni molar ratio of 6:4. Cu_xMn_y ($x = 1-5$, $y = 1-4$) mixed oxides [50] in combination with TEMPO (2,2,6,6-tetramethyl-piperidyl-1-oxyl). Cu–Mn oxide/C (10 wt%) catalytic system in combination with TEMPO (5 mol%) was developed by Yang et al. [51] for oxidation of alcohols with molecular oxygen. Tang et al. [52] reported mixed Cu–Mn oxides catalyst supported on alumina for the oxidation of benzyl alcohol using molecular oxygen. They obtained 90.9% conversion in 4 hrs at 373 K.

Recently, we have reported [53] that copper-manganese oxide with Cu/Mn = 1:4 has higher catalytic activity than that of Cu/Mn = 1:1 for the oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. Herein we report further evaluation of the catalytic efficiency and characterization of mixed copper-manganese CuMn_2 oxide with Cu/Mn molar ratio of 1:2. This mixed oxide exhibits excellent catalytic efficiency with specific activity of $15.04 \text{ mmol g}^{-1} \text{ h}^{-1}$ and yields 100% conversions with 99% selectivity within a short time for selective liquid-phase oxidation of benzyl alcohol to benzaldehyde with molecular oxygen.

2. Experimental

2.1. Catalyst Preparation. Copper-manganese oxide solid solution was prepared by a facile precipitation method employing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and Na_2CO_3 as described in the literature [53]. All reagents used were analytical grade and purchased from MERCK and BDH Chemical Ltd. and used without further purification. The powder oxide was calcined at 300°C in air for 12 h and used for oxidation. The catalysts were prepared with the nominal composition of CuMn_2O_4 , while chemical analyses indicated that the chemical formula of the final product was $\text{CuMn}_{1.87}\text{O}_{4.07}$.

2.2. Techniques Used for Characterization. Scanning electron microscopy (SEM) together with elemental analysis (energy dispersive X-ray analysis: EDX) analysis was conducted on Jeol-SEM model JSM 6360A (Japan). X-ray powder diffraction pattern was recorded on a diffractometer (Rigaku, Ultima IV) at 40 kV and 40 mA using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) for samples precalcined at 300°C. Diffraction data were collected from 5 to 70° with continuous mode, scan speed 2 deg./min, and sampling width 0.02 deg. The surface area was measured using low-temperature nitrogen adsorption by Brunauer-Emmett-Teller (BET) method on a NOVA 4200e surface area and pore size analyzer. Transmission electron microscopy (TEM) was carried out using Jeol TEM model JEM 1101. The infrared spectra were recorded as KBr pellets using a Parkin-Elmer 1000 FT-IR spectrophotometer. The infrared region of the spectrum recorded was in the region of 4000–400 cm^{-1} . Thermogravimetric analysis (TGA) was carried out using Perkin-Elmer Thermogravimetric analyzer 7. Temperature-programmed oxidation (TPO) and temperature-programmed reduction (TPR) profiles were obtained using Micromeritics Autochem 2 Chemisorption Analyzer (model no. 2920, V4.01). The experiments were carried out under oxygen flow 30 (mL/min) in the temperature range from room temperature to 600°C with a heating rate of 10°C/min.

2.3. Oxidation Reaction and Product Analysis. The synthesized copper-manganese mixed CuMn_2 oxide was tested as catalyst in liquid-phase oxidation of benzyl alcohol using molecular oxygen. The reaction was carried out under atmospheric pressure in a three-necked flask connected with oxygen gas cylinder and condenser. In a typical catalytic experiment, a certain amount of catalyst, 2 mmol benzyl alcohol, and 10 mL toluene as solvent were added to the flask. The mixture was then heated to 100°C using an oil bath. Oxygen was bubbled at a flow rate of 20 mL/min into the mixture with continuous stirring using magnetic bar once the reaction temperature was attained. The reaction temperature was maintained at 100–102°C. A small amount of reaction mixture was collected every 10 min. 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

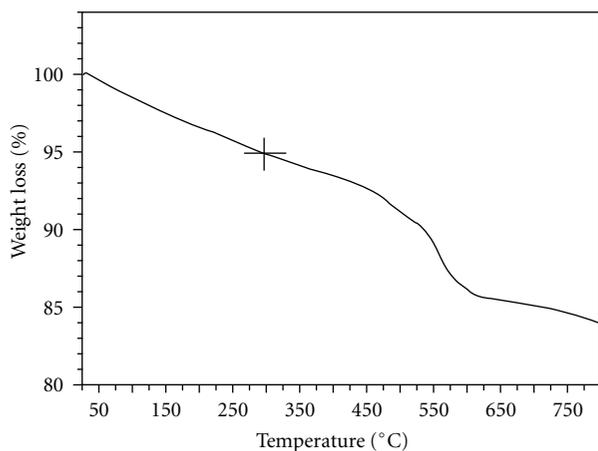


FIGURE 1: TGA profile of mixed CuMn_2 oxide.

conversion of benzyl alcohol and the selectivity to benzaldehyde were calculated by the peak area.

3. Results and Discussion

3.1. Characterization of Mixed CuMn_2 Oxide Catalyst

The morphology of the catalysts was studied with a combination of various characterization techniques. The thermal stability of CuMn_2 oxide determined by thermogravimetric analysis (TGA) is shown in Figure 1. TGA curve of the catalyst shows no significant weight loss up to 300°C , suggesting thermal stability of the compound up to 300°C . The loss of wt% in the temperature $25\text{--}300^\circ\text{C}$ is observed to be 5% which is due to removal of surface-absorbed water or bound water in the structure of the oxide. The presence of water in the catalyst was also detected by IR spectroscopy. The noticeable step of thermal decomposition is observed between 425° and 625°C with a loss of wt.% 7.6. This loss of wt. in this temperature range may be due to decomposition of one or more existing phases and/or formation of Mn_2O_3 phase. The total loss of weight was observed to be 16.08 % when the catalyst was heated up to 800°C . It can be concluded that the catalyst is thermally stable up to $>300^\circ\text{C}$.

X-ray diffraction pattern (Figure 2) of the mixed CuMn_2 oxide precalcined at 300°C shows a mixture of three phases with cubic CuMn_2O_4 (ICSD no. 93434), hexagonal MnO_2 (ICSD no. 76430), and monoclinic CuO (ICSD no. 92368). Peaks of the corresponding phases are indicated by different symbols in Figure 2. Some peaks of cubic CuMn_2O_4 phase are not apparent, but an influence in peak intensity/width of coexisting phase can be detected. The less visible peaks can be attributed to the formation of very little amount of CuMn_2O_4 phase. These peaks might be clearly visible with diffraction pattern having higher resolution and strong intensity, like synchrotron X-ray diffraction pattern. Mn_2O_3 and MnCO_3 phases, which were detected in our earlier studies [53] in CuMn_4O_4 ($\text{Cu}:\text{Mn} = 1:4$), were not detected in the present sample by X-ray diffraction. It is seen in the diffraction

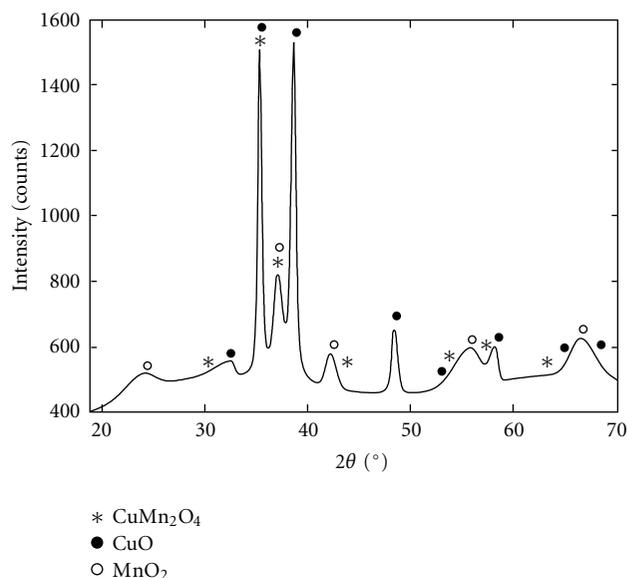


FIGURE 2: Powder X-ray diffraction pattern of mixed CuMn_2 oxide. Each symbol indicates peak of the corresponding phases.

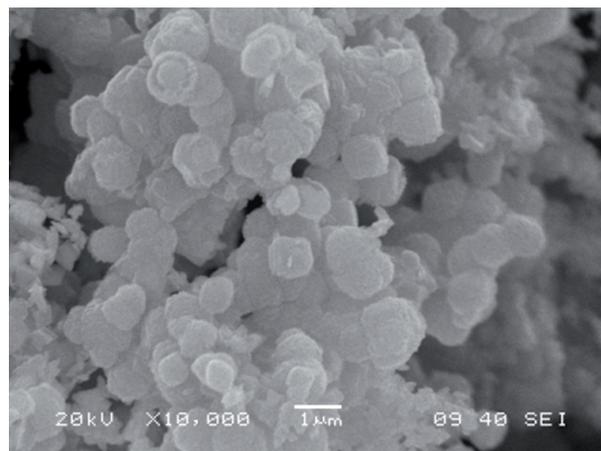


FIGURE 3: Scanning electron microscopy (SEM) image of mixed CuMn_2 oxide precalcined at 300°C .

pattern that peaks of MnO_2 are broader, suggesting an amorphous nature of this phase. The crystallite size of the catalysts was determined from XRD line broadening (determined using the Scherrer equation) using peaks appeared at 35.62 , 37.40 , 38.88 , 42.47 , and 48.69 in 2θ since these seem to be single peak. Furthermore, better result is often obtained using single peak, and peaks appeared between 30 and 50° in 2θ . The average crystallite size was obtained to be 29.26 nm by averaging the size obtained from the five peaks. The higher specific activity of the catalyst may be attributed to the formation of amorphous MnO_2 and/or small crystallite size of the mixed oxide.

Figure 3 shows images of scanning electron microscopy (SEM) of the mixed CuMn_2 oxide after calcinations at 300°C . A uniform spherical morphology with the average diameter being ca 900 nm was observed. The surface area of the mixed

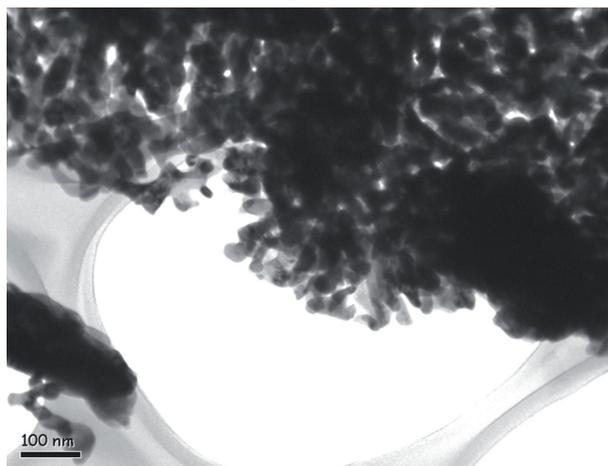


FIGURE 4: Transmission electron microscopy (TEM) image of mixed CuMn_2 oxide precalcined at 300°C .

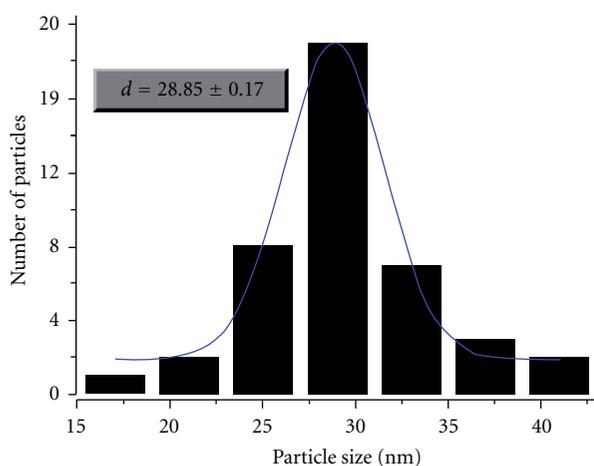


FIGURE 5: Particle size distribution determined from TEM images of mixed CuMn_2 oxide precalcined at 300°C .

CuMn_2 oxide was obtained to be $101.86\text{ m}^2/\text{g}$ through BET analysis.

TEM images of the catalyst (Figure 4) showed no indication of the existence of a unique phase and are not well crystalline. Copper and manganese oxides as well as other species were distributed over all the area.

Particle size distribution calculated from the TEM image (Figure 4) using ImageJ 1.44 [54] is shown in Figure 5. Mean particle size was obtained to be $28.85 \pm 0.17\text{ nm}$, which is in good agreement with the crystallite size determined by Scherrer equation using XRD line broadening (29.26 nm).

In Figure 6, FT-IR spectrum of the mixed CuMn_2 oxide is shown. The IR band appearing at 3431 cm^{-1} may be due to the presence of OH group and H_2O as bound water in the structure. The absorption band at 1636 cm^{-1} corresponds to bending vibration modes of combined water molecules. The presence of absorption band at 582 and 536 cm^{-1} may be assigned to vibration of Cu-O in monoclinic CuO. Morales et al. [55] observed similar bands in copper-manganese

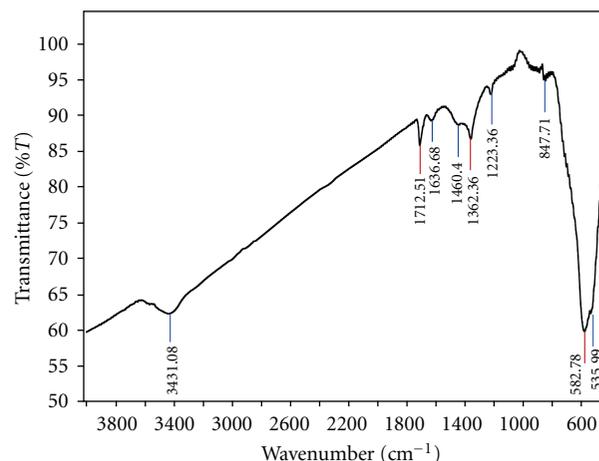


FIGURE 6: Fourier transform infrared (FTIR) spectroscopy of mixed Cu-Mn oxide (Cu : Mn = 1 : 2) precalcined at 300°C .

mixed oxide. Peaks appearing in the range $1223\text{--}1713\text{ cm}^{-1}$ may be resulting from interactions among Mn, OH, and O atoms/groups. The characteristic bands at ca 672 and 524 cm^{-1} for Mn_2O_3 [56] were not observed, suggesting the absence of Mn_2O_3 phase which is in agreement with the X-ray diffraction pattern.

The TPR profile of the oxide exhibited a large peak centered at 220°C , which may be attributed to the reduction of CuO as X-ray diffraction pattern showed the presence of this phase. This reduction stage was detected for Cu_1Mn_2 oxide [57]. Another weak peak that appeared around 400°C may be reduction from MnO_2 to Mn_2O_3 . TPO profile showed two weak and broad peaks centered at 180° and 300°C . These two stages can be ascribed to the oxidation from MnO to MnO_2 via Mn_3O_4 . Soylu et al. [57] reported similar oxidation stages in 9.5% MnO_2/HCLT .

3.2. Catalytic Performance. The mixed CuMn_2 oxide nanoparticles were synthesized following method described in our previous work [53]. Initially, we examined the effect of calcined temperature at 300°C and 500°C on catalytic performance of mixed CuMn_2 oxide and found that catalyst precalcined at 300°C led to higher performance in liquid-phase selective oxidation of benzyl alcohol with molecular oxygen. In order to determine the effect of catalyst concentration on activity, 300 mg of the mixed CuMn_2 oxide was used as catalyst for 2 mmol of benzyl alcohol. A 100% conversion of benzyl alcohol was obtained within a very short reaction time ($<10\text{ min}$) at 102°C . Benzyl alcohol was converted into benzaldehyde with 100% conversion at 102°C after 20 min in presence of 200 mg catalyst with molecular oxygen. The specific activity for this conversion was determined to be $30.00\text{ mmol g}^{-1}\text{ h}^{-1}$. A longer reaction time (80 min) was required to achieve 100% conversion under the same reaction conditions in presence of 100 mg catalyst. The specific activity obtained using 100 mg of the catalyst was determined to be $15.00\text{ mmol g}^{-1}\text{ h}^{-1}$. With decreasing the amount of catalyst from 200 mg to 100 mg , the specific activity decreased by half to obtain 100% with no change in selectivity to benzaldehyde.

TABLE 1: Catalytic performance in oxidation of benzyl alcohol to benzaldehyde over mixed CuMn₂ oxide using molecular oxygen.

Catalyst (mg)	Time (min)	Conversion of alcohol (%)	Specific activity (mmol·g ⁻¹ ·h ⁻¹)	Selectivity (%)
200	10	85.40	51.24	99
	20	100	30.00	99
100	10	49.02	58.82	99
	20	69.20	41.52	99
	30	81.00	32.40	99
	40	87.74	26.32	99
	50	92.37	22.17	99
	60	95.81	19.16	99
	70	98.17	16.83	99
	80	100	15.00	99

Reaction conditions: 100 mg catalyst, 2 mmol benzyl alcohol in 10 mL toluene, and reaction temperature 102°C.

TABLE 2: Comparison of Mn-based catalyst with earlier reported results for its catalytic performance in oxidation of benzyl alcohol to benzaldehyde.

Catalyst	Conversion (%)	Selectivity (%)	Temp. (°C)	Specific activity (mmol·g ⁻¹ ·h ⁻¹)	Reference
MnO ₂	37.7	98.6	80	48.51	[42]
Cu-Mn oxide/C and TEMPO	100	>99	80	15.47	[51]
Cu ₂ Mn-TEMPO	98.8	98.3	120	15.28	[50]
CuMn ₂ oxide	100	99	102	15.00	This work
Mn-Cu-TEMPO	98.0	98.0	20	13.37	[58]
Mn-Fe-HD	53.9	70.6	94	11.21	[36]
Ru/MnO _x /CeO ₂	>99.0	>99	40	9.80	[47]
Amorphous MnO _x -110	72.7	100	110	9.69	[41]
[Mn(bpy) ₂] ²⁺ /HMS	49.2	100	50	9.23	[46]
Mn ₆ Ni ₄ hydroxide	89.0	99	100	8.90	[49]
CuMn ₄ oxide	99	95	102	8.49	[53]
Mn-Cr-HT	18.7	99.5	210	7.23	[37]
H-K-OMS-2	97.0	100	110	4.85	[40]
K-OMS-2	72.0	100	110	3.38	[39]
K(1)Mn(1)/γ-Al ₂ O ₃	72.9	>99	100	2.43	[43]
Mn(1)/γ-Al ₂ O ₃ -p	93.0	>99	100	2.33	[45]
K(2)Mn(1)/C	99.0	>99	100	1.65	[59]
Cu ₁ Mn ₄ /Al ₂ O ₃	90.9	>99	100	1.52	[52]
10 wt.%Mn/AC	42.5	>99	100	1.06	[44]
MnCl ₂ /Montmorillonite-K10	99.0	100	60	0.20	[60]

The selectivity for the oxidation of alcohol to aldehyde was obtained to be >99% for all reactions. It should be noted that, in the absence of catalyst, no detectable conversion of benzyl alcohol was obtained. Also, blank experiment carried out over the catalyst with only solvent toluene (without benzyl alcohol) showed no formation of aldehyde under the same reaction conditions. The conversion of benzyl alcohol, specific activity, and selectivity obtained over the catalyst are mentioned in Table 1 and Figure 7. The initial specific activity gradually decreased, as the catalyst deactivated with reaction time.

The specific activities obtained over the mixed CuMn₂ oxide are about two times higher compared with that of CuMn₄O₄ reported in our earlier study [53]. The mixed CuMn₄ (Cu : Mn = 1 : 4) oxide precalcined at 300°C formed

mainly MnCO₃ and CuO phases, whereas a minor CuMn₂O₄ phase was detected. On the contrary, mixed CuMn₂ oxide was composed of hexagonal MnO₂ and monoclinic CuO with a minor cubic CuMn₂O₄ phases. Therefore, the higher catalytic activity for CuMn₂ oxide can be attributed to the formation of amorphous MnO₂ phase which was not formed in CuMn₄ oxide. The catalytic activity for CuMn₂ oxide may be enhanced by the active MnO₂ phase. The absence of MnCO₃ phase in mixed CuMn₂ oxide which was present in CuMn₄ oxide may also result in higher activity.

The performance in terms of specific activity of mixed CuMn₂ oxide catalyst is compared (Table 2) with those of the Mn-based heterogeneous catalysts reported earlier in oxidation of benzyl alcohol to benzaldehyde. It is seen that Yang et al. [42] reported solvent-free oxidation of

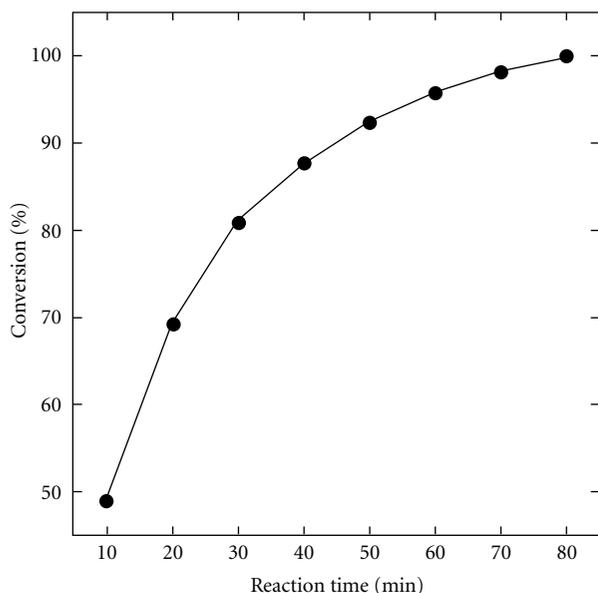


FIGURE 7: Oxidation of benzyl alcohol to benzaldehyde over mixed CuMn_2 oxide precalcined at 300°C . (100 mg catalyst, 2 mmol benzyl alcohol in 10 mL toluene, and reaction temperature 102°C).

benzyl alcohol to benzaldehyde under controlled microwave irradiation manganese oxide MnO_2 having the highest specific activity $48.51 \text{ (mmol g}^{-1} \text{ h}^{-1})$. This specific activity ($48.51 \text{ mmol g}^{-1} \text{ h}^{-1}$) was obtained with 37.7% conversion after 3 h, which is less compared to the specific activity $58.82 \text{ (mmol g}^{-1} \text{ h}^{-1})$ obtained with 49.02% conversion after 10 min in the present study (Table 1). It can be considered that when MnO_2 coexists in CuMn_2 oxide it showed higher catalytic activity than that of pure MnO_2 . This higher activity can be attributed to the synergic effect between MnO_2 and mixed CuMn_2 oxide.

The mixed CuMn_2 oxide provided the specific activity at a complete conversion (100%) is almost the same as that catalyzed by TEMPO-supported Cu_2Mn oxide [50] at 98.8% conversion. The specific catalytic activity ($15.00 \text{ mmol g}^{-1} \text{ h}^{-1}$) of the mixed CuMn_2 oxide is comparable with that of C-(10 wt%) and TEMPO-(5 mol%) supported Cu-Mn oxide [51] ($15.47 \text{ mmol g}^{-1} \text{ h}^{-1}$) at a complete conversion (100%). Among all other Mn-based catalysts listed in Table 2, the mixed CuMn_2 oxide prepared by facile method showed excellent catalytic activity without any support/influence of TEMPO, C, HT, or others (Table 1) at a complete conversion (100%) of benzyl alcohol.

4. Conclusions

The mixed CuMn_2 oxide nanoparticles prepared by a facile coprecipitation method were found to exhibit excellent catalytic activity and selectivity for oxidation of benzyl alcohol to benzaldehyde using molecular oxygen. The mixed CuMn_2 oxide precalcined at 300°C showed high specific activity of $15.04 \text{ mmol g}^{-1} \text{ h}^{-1}$ with a complete conversion (100%) of

benzyl alcohol and 99% selectivity to benzaldehyde within a short reaction period. The X-ray diffraction pattern of the mixed CuMn_2 oxide precalcined at 300°C indicated that the compound is composed of a mixture of hexagonal MnO_2 and monoclinic CuO phases including a minor cubic CuMn_2O_4 phase. The excellent catalytic activity of this mixed oxide can be attributed to the formation of active amorphous MnO_2 phase. Absence of less active Mn_2O_3 and/or MnCO_3 phases in mixed CuMn_2 oxide can be considered as another reason for its higher activity.

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