CATALYTIC PERFORMANCE OF COPPER-MANGANESE SUPPORTED ON ACTIVATED CARBON SYNTHESIZED BY DEPOSITION-PRECIPITATION METHOD

Melody Kimi[1, ✉], Bibie Nur Syafiqah Safiuddin[2], Suh Cem Pang[2]

Abstract. $CuMn_x$/activated carbon (AC, $x = 0.1$, 0.2, 0.5 and 1) nanoparticles were prepared by deposition-precipitation method. The catalytic performance of $CuMn_x$/AC catalysts were studied for the oxidation of benzyl alcohol to benzaldehyde. The molar ratio of Mn plays an important role in the catalytic performances. The optimum amount of Mn is 0.1 with the highest benzyl alcohol conversion of 63 %.

Keywords: benzyl alcohol oxidation, bimetallic catalyst, activated carbon, copper, manganese.

1. Introduction

Selective catalytic oxidation of alcohols to produce the corresponding aldehydes and ketones, in particular, benzyl alcohol to benzaldehyde has been regarded as one of the most important organic transformations in industrial chemistry [1, 2]. Benzaldehyde has been widely applied in the manufacture of odorants, flavours and pharmaceutical intermediates as an important raw material [3]. It is generally prepared in the industry either by hydrolysis of benzyl chloride or by oxidation of toluene [4]. Environmental concern has forced researchers to explore benign synthetic methods. Therefore, many new processes for benzaldehyde synthesis have emerged and catalytic oxidation of benzyl alcohol to benzaldehyde has attracted much attention both in laboratory and chemical industry. The usage of heterogeneous catalyst for the liquid-phase selective oxidation of benzyl alcohol under mild conditions has attracted attention from the viewpoint of sustainable chemical processes [5, 6].

Solid catalysts used for the catalytic oxidation of benzyl alcohol to benzaldehyde include metals [7, 8], metal oxides [9] and supported metals or metal oxides [10, 11]. The use of transition metals such as Cu [12, 13] and Mn [9, 14, 15] containing catalysts offer a good alternative in comparison to the expensive noble metals. Choudhary *et al.* [12] have tested the performance of Cu containing hydrotalcite-like solid catalysts with 41 % conversion for the oxidation of benzyl alcohol [12]. Encapsulated Cu(II) complexes in zeolite-Y also showed a conversion of 29 % for similar reaction [16]. Manganese oxide is extensively studied because of its strong oxygen storage/release ability, excellent redox properties and low cost [17, 18]. Manganese oxide was reported as a superior catalyst for the aerobic oxidation of benzyl alcohol in liquid-phase with up to 100 % selectivity [19]. The catalytic activity of Mn species was very much dependent on the oxidation state [20].

Supported metal catalyst has been proven to improve the selective conversion of benzyl alcohol to benzaldehyde by oxidation reaction. The use of activated carbon (AC) as a catalyst support to immobilised metal catalyst offers advantages such as high surface area and corrosion resistance [21]. Both the texture and surface chemistry of AC support have distinct effect on the catalytic performance of AC supported catalysts [22, 23]. The ability of AC to activate molecular oxygen that is essential for oxidation reaction was also reported [24].

A comparative catalytic study was carried out to evaluate the catalytic performance of $CuMn_x$/AC for the selective oxidation of benzyl alcohol. The catalytic performance in the liquid-phase oxidation of benzyl alcohol with hydrogen peroxide as the oxidant was examined and the influence of Mn mol ratio has been thoroughly investigated. The $CuMn_{0.1}$/AC showed the best catalytic performance, which suggests that the amount of Mn play a crucial role. Typically, a high conversion of 63 % as well as product selectivity of > 99 % was achieved within very short reaction time (2 h) under mild conditions. The characterization results showed the particle size and metal dispersion are dependent on the Mn loading which are then interrelated with the catalytic performances.

[1] Centre for Pre-University Studies, University Malaysia Sarawak, Kota Samarahan, Malaysia
[2] Department of Chemistry, Faculty of Resource Science and Technology,
University Malaysia Sarawak, Kota Samarahan, Malaysia
✉ kmelody@unimas.my

2. Experimental

2.1. Catalysts Preparation

The $CuMn_x/AC$ ($x = 0.1, 0.2, 0.5, 1$) nanoparticles catalyst were prepared by using homogeneous deposition-precipitation method previously reported with slight modification [25, 26]. In brief, for the synthesis of $CuMn_{0.1}/AC$ catalyst, 1.0 g of AC was added to 50 ml aqueous solution of 0.1 mol of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.01 mol of $Mn(NO_3)_2 \cdot 4H_2O$ under stirring at room temperature. The resulting mixture was stirred for 15 min and $0.1 \ mol \cdot l^{-1}$ of NaOH was added dropwise, under vigorous stirring at room temperature until the pH became 10.0. The resulting solution was kept at room temperature for 24 h, centrifuged and washed with deionized water until neutral pH. The prepared sample was dried at 383 K overnight followed by calcination at 823 K in air for 3 h. To compare the catalytic activities, single metal catalyst Cu/AC and Mn/AC catalysts were also prepared using the same method.

2.2. Catalysts Characterisation

X-ray diffraction (XRD) patterns of the catalysts were obtained by D8 Advance (BRUKER AXS, Germany) diffractometer using Cu Kα radiation ($\lambda = 1.541$ Å) from 20° to 70° to investigate the structural properties. Scanning Electron Microscope (SEM) images were taken using JSM-6390 (JEOL, USA) to identify the morphology and estimate the particle size of the catalysts. Transmission electron microscopy (TEM) photographs were taken with a JEOL JEM-2999FMII apparatus. Samples for TEM were prepared by placing a drop of a colloidal dispersion of catalyst in an ethanol solvent onto a perforated copper grid, followed by naturally evaporating the solvent. The mean particle diameters were calculated by nano measurer software from TEM image analysis.

2.3. Evaluation of Catalytic Performance

Liquid phase oxidation of benzyl alcohol was carried out using procedures that were reported previously with slight modification [27]. In a typical reaction, 2.6 ml (25 mmol) of benzyl alcohol, 3.3 ml (32 mmol) of 30 % H_2O_2 and 0.1 g of the catalyst powder were loaded in a 50 ml double neck round bottom flask containing 20 ml of toluene as solvent. The flask was connected to a reflux condenser, magnetically stirred and kept in an oil bath at 353 K for 2 h. After reaction, the solid catalysts were separated by centrifugation and the liquid samples were filtered and analysed by gas chromatography to evaluate the products by GC-MS (SHIDMADZU QP 5000) equipped with a flame ionization detector (FID) and a medium polarity capillary column (BPX-5 column (29.4 m×0.25 mm), with film thickness of 0.25 μm and with helium as the carrier gas.

3. Results and Discussion

3.1. Crystal structure of catalysts

X-ray diffraction was employed to analyse the effect of Mn addition into Cu/AC and the amount of Mn on the crystalline structure and phase of the samples. XRD patterns of the single metal Cu/AC, Mn/AC and $CuMn_x/AC$ ($x = 0.1, 0.2, 0.5$ and 1) samples were shown in Fig. 1. The weak diffraction peak at $2\theta = 26.5°$ observed for all the samples was assigned to the activated carbon support [28] with hexagonal phase according to PDF no. 01-071-3739. For Cu/AC sample, three major peaks could be observed at $2\theta = 35.5°$, 38.7° and 48.7° which were attributed to (111) and (202) planes, respectively, for CuO hexagonal phase. The peaks are in good agreement with PDF no. 00-045-0937. There were also impurity peaks observed at $2\theta = 36.4°$ and 42.3° that correspond to (111) and (200) of Cu_2O. As for Mn/AC sample, two major diffraction peaks at $2\theta = 32.3°$ and 36.0° correspond to (103) and (211) planes of Mn_3O_4 tetragonal phase with PDF no. 01-089-4837.
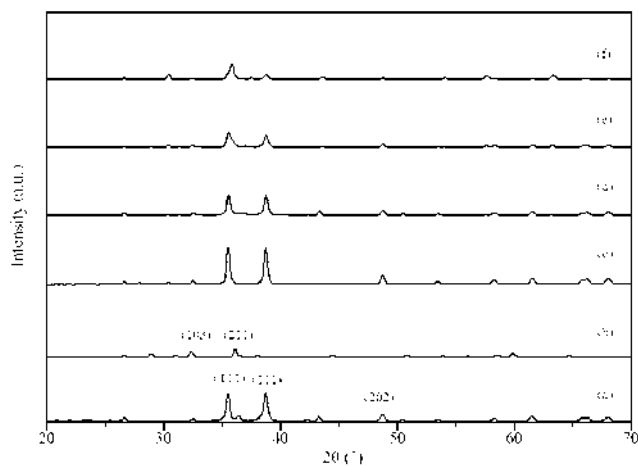

Fig. 1. Powder XRD pattern of Cu/AC (a), Mn/AC (b), $CuMn_{0.1}/AC$ (c), $CuMn_{0.2}/AC$ (d), $CuMn_{0.5}/AC$ (e) and $CuMn_1/AC$ catalyst (f)

All $CuMn_x/AC$ samples had peaks that correspond to hexagonal CuO. Due to the weak crystalline peaks of Mn_3O_4, it was not observed in $CuMn_x/AC$ samples, although the characteristic peaks for Cu and Mn were quite close to distinguish. This also indicates high dispersion of Mn particles over the catalyst surface [29]. An influence in

peak intensity of coexisting phase between CuO and Mn_3O_4 can be detected. Peaks corresponding to Cu_2O also disappeared with the addition of Mn. $CuMn_{0.1}$/AC peak intensity increased compared to Cu/AC, indicating the improvement in the crystallinity. As the amount of Mn increased, $CuMn_x$/AC catalysts exhibited broader characteristic peaks than those of Cu/AC. This showed that the addition of Mn affected the crystallinity of the samples. The changes in the crystalline peaks implied that $CuMn_x$/AC catalyst was formed. It can be deduced that Mn had entered the lattice of CuO [30]. There were no changes in crystal phase of CuO with the addition of Mn into Cu/AC catalyst. This result evidences that the crystal phase of CuO is not influenced by the addition of Mn. The addition of Mn at irrespective amount also did not lead to distortion of the CuO phase.

With increasing Mn content, the peaks corresponding to CuO slightly shifted to higher angle. The peaks shift indicates that Mn^{2+} (0.80 Å) with the larger ionic radius have entered into the CuO lattice to replace Cu^{2+} (0.72 Å) ions of smaller ionic radius. The peak shift and crystal shrinking indicated that Mn may alloy with Cu to change the crystal lattice of Cu. Similar observation was reported when Bi was added into Pt/CNT [31], which resulted in good contact and synergic effect with each other.

The crystallite size of the catalysts calculated using Scherrer's equation from the broadening of the peak corresponding to the (111) plane and *d*-spacing are tabulated in the Table. The crystallite size of CuO was found to be smaller compared to Mn_3O_4 due to the smaller ionic radius of Cu^{2+}. As for $CuMn_x$/AC catalysts, the crystallite size range is around 26–35 nm, which is between the size for both single metal catalysts. There was not much difference in the crystallite sizes when the amount of Mn increased. The slight decrease in crystallite size could be due to defects caused by the addition of Mn. The *d*-spacing of the catalysts also did not differ much as the amount of Mn increased.

3.2. Morphology of catalysts

The morphology and structure of the catalysts were analysed using scanning electron microscope (SEM). Fig. 2a shows Cu/AC samples, which have an estimated diameter of 0.40–1.00 µm. The AC surfaces are filled with many small and spherical dots of Cu. This showed that Cu is widely distributed on the surface of AC. Mn/AC (Fig. 2b) showes aggregated particles with irregular shape on AC surface in the size range of 0.30–1.00 µm. The addition of Mn on Cu/AC catalyst (Figs. 2c-2f), showed small sphere particles that are well defined in the range of 0.40–0.50 µm. There were no considerable changes in the particle shape and sizes when the amount of Mn added increased. However, the addition of Mn changes the morphology of the catalyst which differs from both CuO and Mn_3O_4. Thus, the presence of Mn formed a synergistic interaction with Cu/AC. The slight decrease of the particles size of Cu/AC catalyst when Mn was added could be attributed to the interactions between two metals, known as stabilizing effect [32] as confirmed by XRD. The dispersion of the particles was more uniform as compared to monometallic Cu/AC catalyst. Figs. 2c-2f also show that $CuMn_x$ particles have large contact area with AC support.

The TEM images of $CuMn_{0.1}$/AC catalysts shown in Fig. 3 indicate that the Cu and Mn species are distributed uniformly over the surface of AC. It shows that deposition-precipitation method for the synthesis of catalyst prevents the agglomeration of nanoparticles. The particles size of Cu and Mn species calculated by nano measure is in the range of 0.2–0.4 µm, which is similar with SEM. It is worth noting that particle size calculated by TEM is larger than the values calculated by the Scherrer equation. Imaging techniques such as TEM and SEM give the size of the particle, while XRD disclose the size of the crystallite [33].

3.3. Catalytic Performances

The performance of single metal Cu/AC, Mn/AC and various $CuMn_x$/AC (x = 0.1, 0.2, 0.5 and 1) on the oxidation of benzyl alcohol at 353 K for 2 h with H_2O_2 as oxidant are summarized in the Table. Pure AC did not show considerable activity for alcohol oxidation. All supported metal catalysts showed catalytic activity with 100 % selectivity to produce benzaldehyde under the conditions applied. It was deduced that the surface of AC was used for oxygen activation and regeneration [34] while metal oxides have strong ability towards alcohol dehydrogenation [24].

Properties and catalytic activity of the catalyst

Entry	Catalyst	*d*-Spacing, nm	Crystallite size, nm	Conversion, %
1	Cu/AC	2.3241	29.4	49.9
2	Mn/AC	2.3632	41.6	32.8
3	$CuMn_{0.1}$/AC	2.3243	35.7	63.0
4	$CuMn_{0.2}$/AC	2.3226	32.8	58.2
5	$CuMn_{0.5}$/AC	2.3226	26.0	54.9
6	$CuMn_1$/AC	2.3223	28.9	44.3

Reaction conditions: 0.1 g catalyst, 2.6 ml benzyl alcohol, 3.3 ml H_2O_2, 20 ml toluene as a solvent, T = 353 K, t = 2 h.
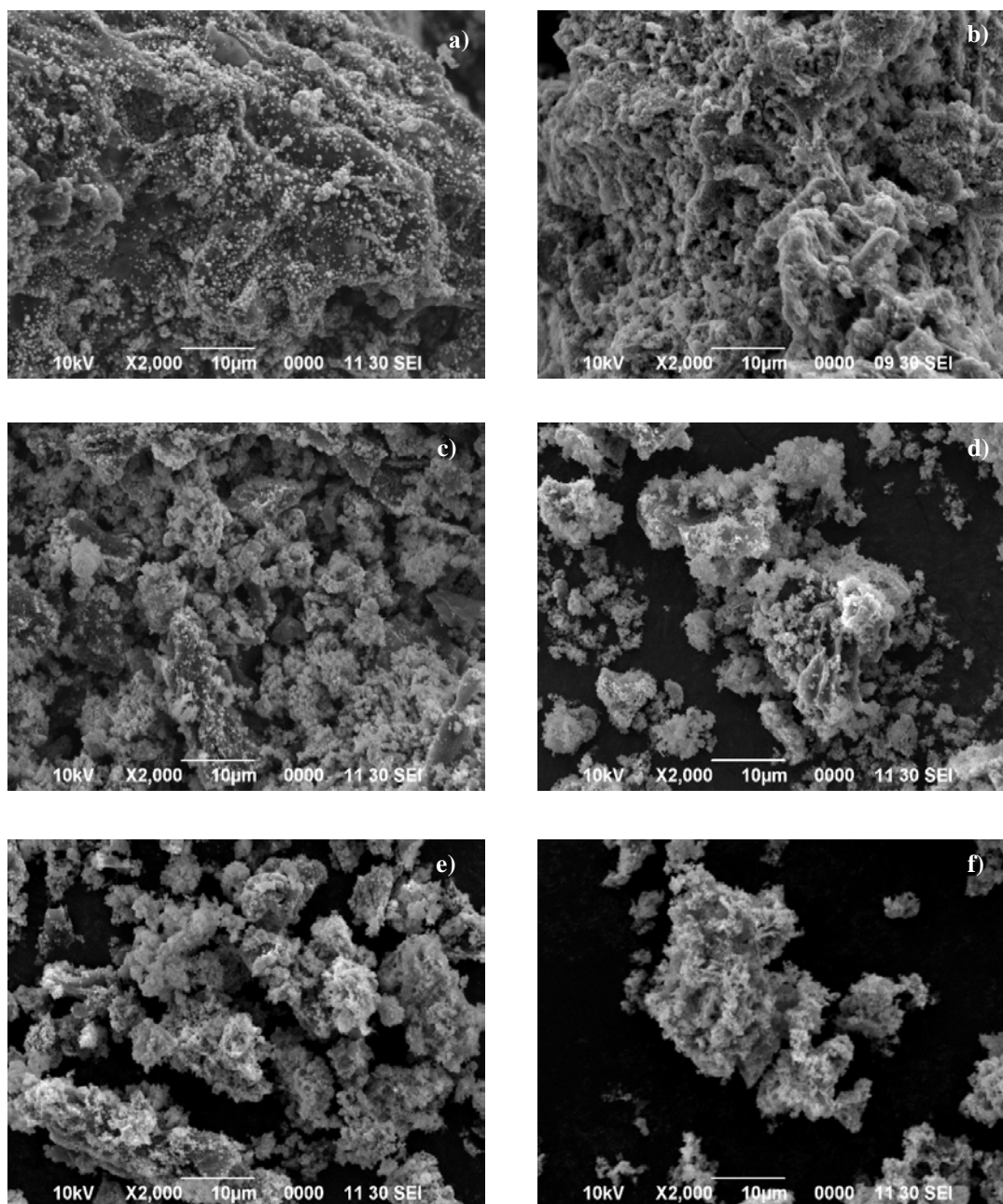
Fig. 2. SEM images of Cu/AC (a), Mn/AC (b), $CuMn_{0.1}$/AC (c), $CuMn_{0.2}$/AC (d), $CuMn_{0.5}$/AC (e) and $CuMn_1$/AC (f) catalyst
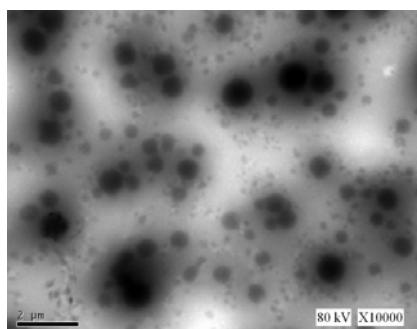

Fig. 3. TEM images of $CuMn_{0.1}$/AC

From XRD analysis, it can be assumed that the CuO and Mn_3O_4 is highly dispersed on the AC as the support. This produced synergistic effect when combined. For monometallic Cu/AC, the conversion of benzyl alcohol was 49.9 %. Single metal Mn/AC also showed low conversion of benzyl alcohol. Upon the addition of Mn into Cu/AC, the catalytic activity improved greatly. Different Mn content resulted in differences in the catalytic performances. The best result was obtained with $CuMn_{0.1}$/AC catalyst, which gave 63.0 % conversion of benzyl alcohol. This effect can be explained by the better crystallinity of this catalyst compared to the others. High crystallinity could be deduced to provide large number of active sites due to higher metal dispersion. The other bimetallic catalyst had slightly higher conversion of benzyl alcohol compared to their monometallic catalyst. However, with further raising the concentration of Mn until Cu/Mn = 1/1, the catalytic activity gradually decreases. The activity of $CuMn_1$/AC was even lower than the activity of monometallic Cu/AC. It was reported that in a bimetallic system of Cu and Au, Cu played significant role in activating oxygen and evidence of electron transfer from Cu was observed [35]. The synergistic effect originates mainly from the electronic effect in which Cu and Mn transfer electron and assists to activate oxygen. The highly dispersed manganese species, coexistence of Mn^{2+} and Mn^{3+}, were postulated to be the active sites [36] in addition to Cu^{2+}. However, when too much Mn was added, agglomeration of particles could deter the smooth transfer of electrons [20]. Hence, the particle size and distribution of the active metal species can be tuned by changing the mol ratio of Mn added. The deposition-precipitation techniques had been shown to afford high dispersion and narrow distribution of metal nanoparticles size [37]. High dispersion of metal active sites provides high accessibility of the reactants [9] to the catalyst, which resulted in high catalytic performances in optimum amount.

4. Conclusions

A series of Cu-Mn_x/AC catalysts was successfully prepared with deposition-precipitation method. Their catalytic performances were evaluated in the oxidation of benzyl alcohol using hydrogen peroxide as oxidant. Highly dispersed Cu and Mn particles were attached to the surface of AC when the molar ratio of Mn is 0.1. $CuMn_{0.1}$/AC possesses the best catalytic activity with 63 % conversion after 2 h. The addition of small amount of Mn had contributed to the high crystallinity of the catalyst which would enhance the catalytic activity by suppressing the agglomeration of Mn. When Mn loading was above the optimum amount, it decreased Mn dispersion. This will reduce the active metal surface.

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ХАРАКТЕРИСТИКА МАРГАНЕЦЬ-МІДНОГО КАТАЛІЗАТОРА НА АКТИВОВАНОМУ ВУГЛЕЦІ, СИНТЕЗОВАНОМУ МЕТОДОМ ВИСАДЖЕННЯ

Анотація. *Наночастинки СиМnₓ/активоване вугілля (АВ, x = 0,1; 0,2; 0,5 і 1) отримували методом висадження. Вивчено каталітичну характеристику СиМnₓ/АВ для окиснення бензилового спирту до бензальдегіду. Показано, що молярне співвідношення Mn відіграє важливу роль у каталітичній характеристиці. Оптимальна кількість Mn становить 0,1 при максимальному перетворенні бензилового спирту 63 %.*

Ключові слова: *окиснення бензилового спирту, біметалічний каталізатор, активований вуглець, мідь, марганець.*