

## Deposition-Precipitation Synthesized CuCo/Activated Carbon Catalysts for Benzyl Alcohol Oxidation Reaction

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The effect of  $\text{Co}_x$  addition in the range of 0.1-1 mol into Cu supported on activated carbon (AC) catalysts fabricated by deposition-precipitation method was assessed.  $\text{CuCo}_x/\text{AC}$  prepared via the same method under different calcination temperatures was studied to evaluate the properties and activity of the catalysts. The bimetallic Cu-Co catalysts are structurally characterized by X-ray diffraction and scanning electron microscopy. It was found that Co is well incorporated in Cu/AC lattice and improves the crystalline structure with optimum Co loading.  $\text{CuCo}_x/\text{AC}$  nanoparticles formed with uniform shapes and size under the present synthesis conditions. The catalytic performances of the as-prepared catalysts were evaluated towards the aerobic oxidation of benzyl alcohol using hydrogen peroxide as the oxidant. Cu/AC, Co/AC and  $\text{CuCo}_x/\text{AC}$  showed ability to oxidize benzyl alcohol to benzaldehyde.  $\text{CuCo}_{0.2}/\text{AC}$  calcined at 450 °C showed the highest catalytic activity with 86% conversion of benzyl alcohol due to the high crystallinity compared to the monometallic counterpart. It was found that the crystallinity of the catalysts could be tuned by varying the amount of Co. The synergistic effects of Cu-Co in optimum mole ratio and calcination temperature influenced the availability of active sites participating in the catalytic activity.

**Keywords:** CuCo/activated carbon, Catalyst, Benzyl alcohol, Benzaldehyde, Oxidation

### INTRODUCTION

Production of aldehydes from oxidation of alcohols has been extensively researched [1] as these aldehydes are valuable intermediates for industries such as fragrance, food additives and pharmaceuticals [2]. In search for oxidation process that are capable of overcoming the drawbacks of conventional use of excess stoichiometric metal oxidants [3,4], noble metal nanoparticles including Au [5,6] and Pd [7] have been widely recognized as the most efficient catalysts for oxidation reactions. The limited availability and high cost have prompted the use of transition metals such as Cu [8,9] and Co [10,11] as catalyst for the oxidation of benzyl alcohol to benzaldehyde with oxygen or hydrogen peroxide as an oxidant. The presence of weak Co-O bond strength causes the reactivity of  $\text{Co}_3\text{O}_4$  toward oxidation, releasing reactive oxygen species from the lattice structure

[12]. In addition, incorporating another transition metal into  $\text{Co}_3\text{O}_4$  to form bimetallic structure mitigates particle sintering on account of the phase segregation in oxidizing reaction conditions [13]. The interfaces formed from the Cu-Co heterostructures would provide active sites for the activation of oxygen molecules, resulted in the enhanced activity of bimetallic systems for aerobic oxidation reactions [13]. Moreover, structural properties of bimetallic catalysts are easily tuned over a broad range by simply varying the metal composition. In prior studies, bimetallic CuNi catalysts were used to investigate the catalytic conversion for oxidation of benzyl alcohol [14]. As an improvement, in this study Ni is replaced by employing Co as metal dopant, in addition to the tailoring of calcination temperature.

The catalytic activity of transition metal catalysts could be further enhanced by anchoring them to a support. The role of the support is to disperse the active catalysts to achieve high mass activity and prevent the agglomeration of metal oxide catalysts. When the catalysts are well

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distributed, the stability of metallic nanoparticles and synergy to activate reactants through interactions between metal and support itself [15] are greatly improved. The large surface area and chemical stability prompt the use of activated carbon (AC) as the catalytic support in this study [16]. In addition, the presence of phenolic groups can either reduce metal to metal nanoparticles or stabilize the high oxidation states at the same time [17].

The present work aims to assess the optimum mole ratio and calcination temperature of Co loading onto bimetallic  $\text{CuCo}_x/\text{AC}$  catalysts prepared by deposition-precipitation method. The contribution of structural properties of the obtained  $\text{CuCo}_x/\text{AC}$  catalysts was assessed through the oxidation reaction of benzyl alcohol in the presence of  $\text{H}_2\text{O}_2$  as the oxidant under mild conditions.

## EXPERIMENTAL

### Materials

Activated carbon (Darco, 100 mesh) was purchased from Sigma Aldrich. Copper nitrate trihydrate (99.5%, Merck), cobalt nitrate hexahydrate (98%, ACS), benzyl alcohol (EMSURE, Merck), sodium hydroxide pellets (A.R./ACS, R&M), toluene (A.R./ACS, R&M), benzaldehyde (99.5%, Aldrich), ethanol (95%, Hmbg), hydrogen peroxide (30%, A.R., R&M), dichloromethane (A.R., R&M), nitric acid (65%, A.R.), were purchased and used as received without any further purification.

### Preparation of Catalysts

The  $\text{CuCo}_x/\text{AC}$  ( $x = 0.1, 0.2, 0.5, 1$ ) catalysts were prepared using homogeneous deposition-precipitation method previously reported with slight modification [14,18]. Typically, in the synthesis of  $\text{CuCo}_{0.1}/\text{AC}$  catalyst,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.1 mol) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.01 mol) were dissolved in 50 ml of distilled water. AC (1.0 g) was added into the aqueous solution followed by NaOH (0.1 M) dropwise, under vigorous stirring at room temperature until the pH of the solution becomes 10.0. The resulting solution was aged at room temperature for 24 h. Then, the solution was centrifuged and washed with distilled water until the pH of the solution turned into neutral. The prepared sample was dried at 110 °C overnight followed by calcination at 450 °C in air for 3 h. The best mole ratio sample was

additionally calcined at 500 °C and 550 °C to find the optimum calcination temperature. In order to compare the properties, single metal catalyst, Cu/AC and Co/AC were also prepared using the same method.

### Characterisation of Catalysts

The crystal structure of the catalysts was examined by X-ray diffraction (XRD) using D8 Advance diffractometer (BRUKER AXS, Germany) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) in the range of  $10^\circ$ - $80^\circ$ .

The morphologies of the catalysts and particle size estimation were done using scanning electron microscope (SEM) analysis by JSM-6390 (JEOL, USA).

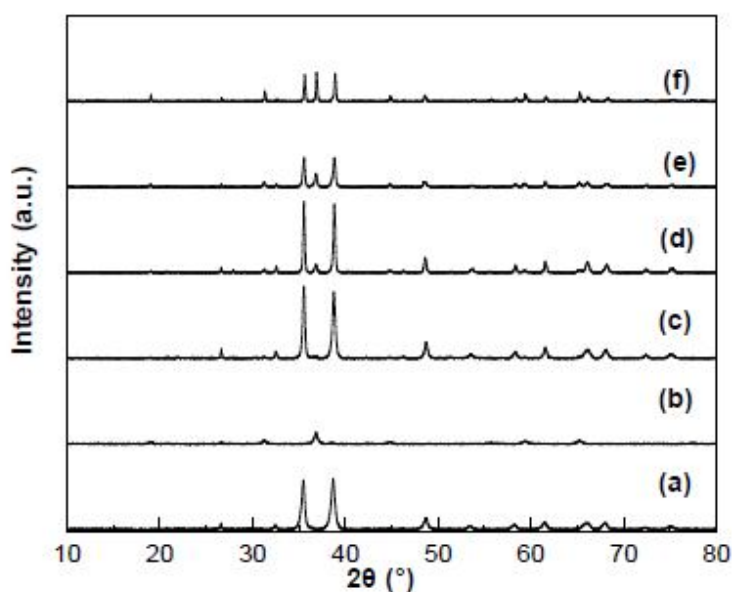
### Catalytic Testing

Liquid phase oxidation of benzyl alcohol was carried out using procedures previously reported with slight modification [19]. In a typical reaction, 2.6 ml (25 mmol) of benzyl alcohol, 3.3 ml (32 mmol) of 30%  $\text{H}_2\text{O}_2$  and catalyst (0.1 g) powder were loaded in a 50 ml double neck round bottom flask containing toluene (20 ml) as the solvent. The flask was connected to a reflux condenser, magnetically stirred and kept in an oil bath at 80 °C for 2 h. After reaction, the solid catalyst was separated by centrifugation and the liquid samples were filtered and analysed by gas chromatography to evaluate the products by GC-MS (SHIMADZU QP 5000) equipped with a flame ionization detector (FID) and a medium polarity capillary column (BPX-5 column (29.4 m  $\times$  0.25 mm), with film thickness of 0.25  $\mu\text{m}$ ) with helium as the carrier gas.

## RESULTS AND DISCUSSION

### Crystal Structures of Catalysts

XRD patterns of Cu/AC, Co/AC and  $\text{CuCo}_x/\text{AC}$  ( $x = 0.1, 0.2, 0.5, 1$ ) series are shown in Fig. 1. The weak diffraction peak at  $2\theta = 26.5^\circ$  was assigned to the activated carbon support [20] with hexagonal phase. The diffraction pattern for Cu/AC (Fig. 1a) has three primary peaks at  $2\theta = 35.5^\circ, 38.7^\circ$  and  $48.7^\circ$ , assigned to the  $(\bar{1}11)$ , (111) and  $(\bar{2}02)$  lattice planes of CuO hexagonal phase [21]. Co/AC (Fig. 1b) has four peaks, corresponding to  $2\theta = 31.3^\circ, 36.8^\circ, 59.5^\circ$  and  $65.2^\circ$  of the (220), (311), (511) and (440)  $\text{Co}_3\text{O}_4$  cubic phase planes. The catalysts did not



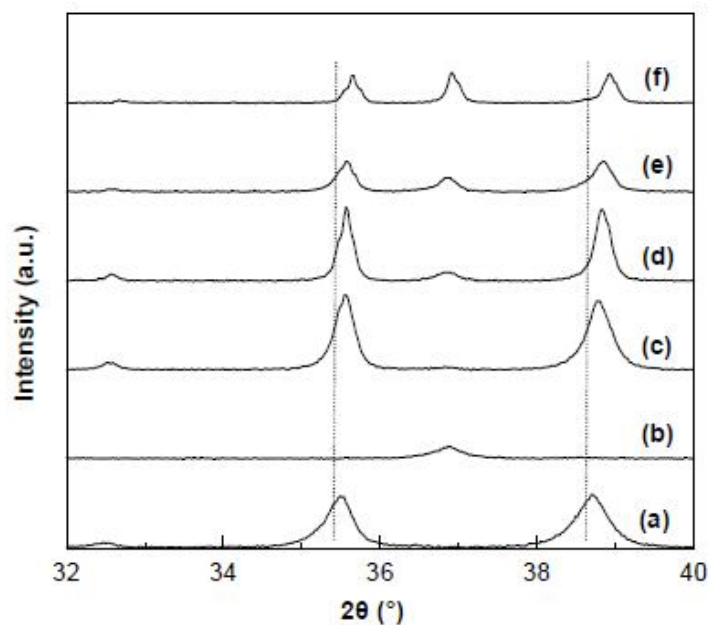
**Fig. 1.** Powder XRD pattern of Cu/AC (a), Co/AC (b), CuCo<sub>0.1</sub>/AC (c), CuCo<sub>0.2</sub>/AC (d), CuCo<sub>0.5</sub>/AC (e) and CuCo<sub>1</sub>/AC (f) catalysts.

show any detectable impurities. The XRD analysis confirms the formation of pure CuO and Co<sub>3</sub>O<sub>4</sub> phases in all four compositions of bimetallic CuCo<sub>x</sub>/AC catalysts prepared. As the amount of Co added increased, the peak intensity corresponding to Co<sub>3</sub>O<sub>4</sub> increased. This confirms the addition of Co into the lattice of CuO. The crystallinity of CuCo<sub>x</sub>/AC catalysts increased when the amount of Co added were 0.1 and 0.2 mol. The highest crystallinity was recorded for CuCo<sub>0.2</sub>/AC. This was followed by a decrease in the crystallinity of the catalysts when the amount of Co added was higher than 0.2 mol. The peaks corresponding to CuO shifted to higher angle as the amount of Co added increased as shown in Fig. 2. The result indicated that the structure of CuO changed with the incorporation of Co into the lattice. This is due to the smaller ionic radius of Co (0.65 Å) compared to Cu (0.72 Å) [22].

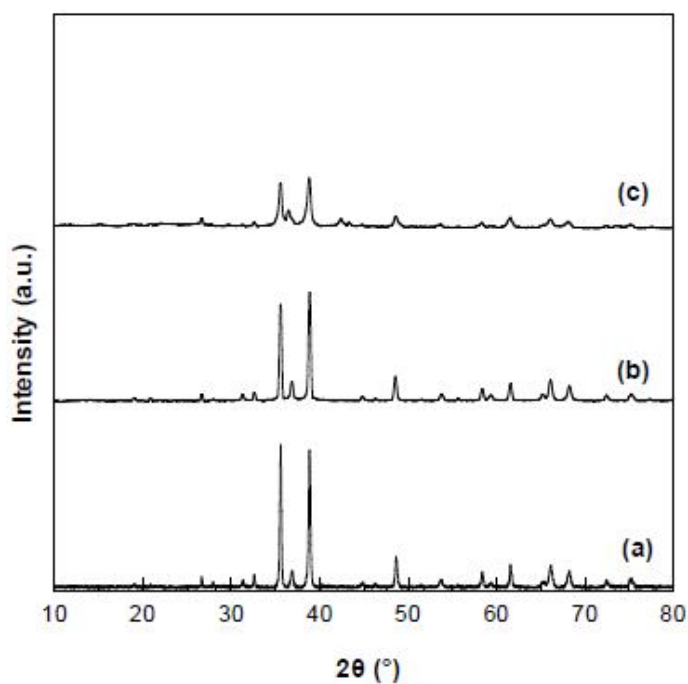
Figure 3 shows the XRD patterns of CuCo<sub>0.2</sub>/AC catalysts synthesized by means of different calcination temperatures at 450 °C, 500 °C and 550 °C. The peaks ascribed to the CuO and Co<sub>3</sub>O<sub>4</sub> phases are obvious regardless of the calcination temperature. With increasing calcination temperature, the peaks corresponding to CuO

become weaker, indicating on a weaker crystallinity and smaller crystallite size. Meanwhile, the peak height corresponding to Co<sub>3</sub>O<sub>4</sub> at 2θ of 37° showed no obvious change. The changes in crystallinity of the catalysts showed that the structure of CuO changed with the incorporation of Co into the lattice corresponding to the calcination temperature.

The crystal diameters of Cu/AC and CuCo<sub>x</sub>/AC were calculated by the Scherrer's equation using the most intense reflection at 38.7° (111), the obtained values are summarized in Table 1. For Co/AC sample, reflection at 36.8° was used to calculate the crystal diameter. The CuCo<sub>x</sub>/AC crystallite sizes decreased as the Co loading increased. Results showed a considerable effect of Co metal oxide dopant on the particle size of Cu/AC and on the sample, respectively. Thus, the presence of Co metal oxide has a characteristic effect on the particles size of the sample. The presence of Co on the surface of Cu in large amount could act as a shield to prevent the growth of the crystal. This is due to the maximum dopants that are able to be accommodated on the crystallite surface to minimize the strain. The segregation of dopants on the surface leads to



**Fig. 2.** Powder XRD pattern of (a) Cu/AC (b) Co/AC (c) CuCo<sub>0.1</sub>/AC (d) CuCo<sub>0.2</sub>/AC (e) CuCo<sub>0.5</sub>/AC and (f) CuCo<sub>1</sub>/AC catalysts from  $2\theta$  of 32° to 40°.



**Fig. 3.** Powder XRD pattern of (a) CuCo<sub>0.2</sub>/AC (450 °C) (b) CuCo<sub>0.2</sub>/AC (500 °C) and (c) CuCo<sub>0.5</sub>/AC (550 °C) catalysts.

**Table 1.** Properties and Catalytic Activity of the Catalyst Synthesized at 450 °C

Entry	Catalyst	d-Spacing (nm)	Crystallite size (nm)	Conversion of benzyl alcohol (%)
1	Cu/AC	2.3241	29.4	49.9
2	Co/AC	2.4361	19.4	54.2
3	CuCo <sub>0.1</sub> /AC	2.3199	36.6	84.2
4	CuCo <sub>0.2</sub> /AC	2.3170	32.0	86.0
5	CuCo <sub>0.5</sub> /AC	2.3168	25.2	81.8
6	CuCo <sub>1</sub> /AC	2.3122	20.9	71.9

\*Reaction conditions: 0.1 g catalyst, 2.6 ml benzyl alcohol, 3.3 ml H<sub>2</sub>O<sub>2</sub>, 20 ml toluene as solvent, T = 80 °C, t = 2 h.

increasing the surface to volume ratio to minimize the energy of the lattice [23]. As a result, the crystallite size is reduced with excess doping.

The crystallite sizes of CuCo<sub>0.2</sub>/AC also decrease with increasing calcination temperature. The results clearly indicated that the growth and crystallization of CuCo<sub>x</sub>/AC had been greatly influenced by calcination temperature. As the calcination temperature increases, the high temperature of combustion reaction and short reaction time enable the formation and evolution of various gases that inhibit the growth of Co<sub>3</sub>O<sub>4</sub> particles resulting in decrease of the crystallite size [24]. Since Co is smaller than Cu, more Co ions could enter the lattice at high temperature resulting in smaller crystallite size [25].

### Morphologies of Catalysts

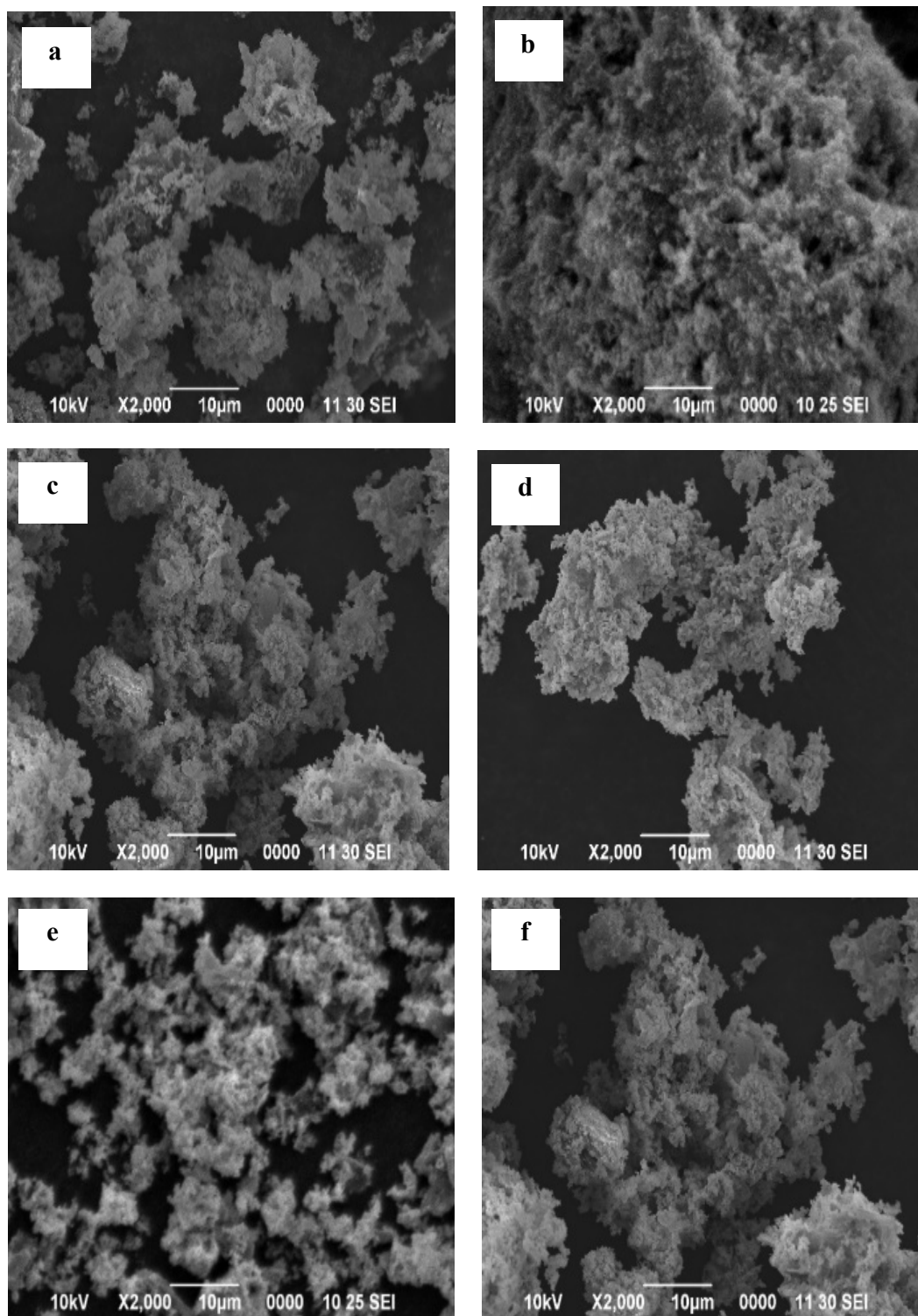
The SEM images of the synthesized catalysts are shown in Fig. 4. According to Fig. 4a, the particles of Cu/AC catalyst were sphere-shaped that agglomerated within a coral structure. The particles diameter is in the range of 0.40-1.10 μm. Co/AC showed more agglomerated sphere-shaped particles compared to Cu/AC. The particle size of Co/AC (Fig. 3b) is in the range of 0.30-0.80 μm, smaller than that of Cu/AC, that is in good agreement with the XRD analysis. The CuCo<sub>x</sub>/AC samples in Figs. 4c-f present a morphology resembling more to Cu/AC as compared to

Co/AC due to the larger amount of Cu in each sample. The general morphology of all CuCo<sub>x</sub>/AC are similar to the coral structure of Cu/AC with less agglomeration compared to single metal Co/AC. The CuCo<sub>x</sub>/AC particle size is estimated in the range of 0.30-0.60 μm. The concentration variation of Co from 0.1 to 1 mole in the CuCo<sub>x</sub>/AC samples did not affect the particle size as well as morphology of CuCo<sub>x</sub>/AC. The surface of AC was not observed due to the large contact area of Cu and Co on the AC support.

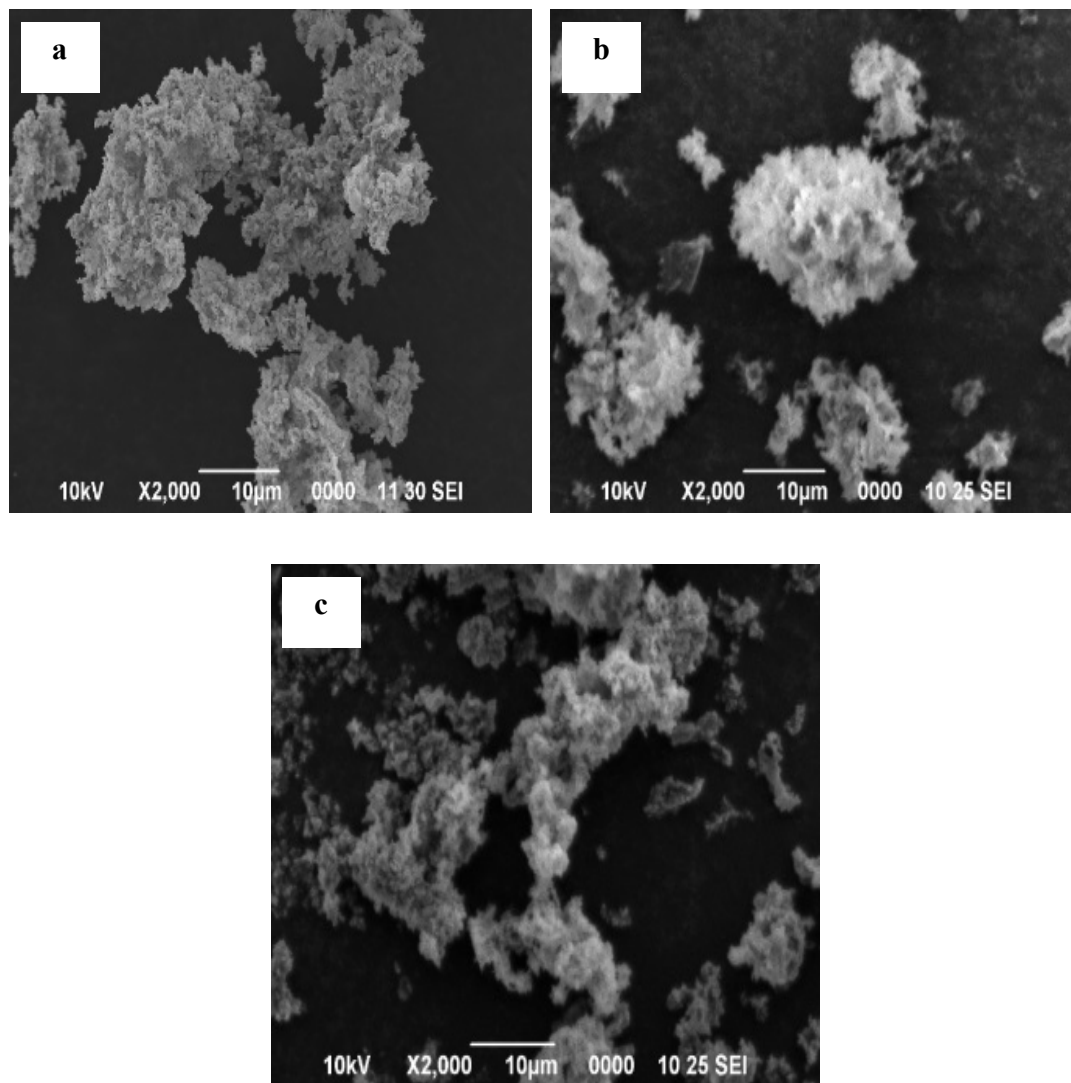
Figure 5 shows the SEM micrograph of CuCo<sub>0.2</sub>/AC obtained at 450 °C, 500 °C and 550 °C, revealing similar morphology and particle size. All the samples comprised of spherical shape particles agglomerated within a coral structure.

### Catalytic Activity

Based on the results in Table 1, all the prepared catalysts Cu/AC, Co/AC and CuCo<sub>x</sub>/AC are active for the oxidation of benzyl alcohol to benzaldehyde. Toluene was used as a non-polar solvent due to inert properties and higher oxygen solubility than alcohols. Furthermore, toluene does not interact with the metal catalysts or compete with reactants to adsorb on active metallic sites [26]. No oxidation reaction occurred in the absence of catalyst with H<sub>2</sub>O<sub>2</sub> acting as the oxidant. The oxidation product of benzyl alcohol using



**Fig. 4.** SEM images of (a) Cu/AC (b) Co/AC (c) CuCo<sub>0.1</sub>/AC (d) CuCo<sub>0.2</sub>/AC (e) CuCo<sub>0.5</sub>/AC and (f) CuCo<sub>1</sub>/AC catalysts.



**Fig. 5.** SEM images of (a) CuCo<sub>0.2</sub>/AC (450 °C) (b) CuCo<sub>0.2</sub>/AC (500 °C) and (c) CuCo<sub>0.2</sub>/AC (550 °C) catalysts.

**Table 2.** Properties and Catalytic Activity of CuCo<sub>0.2</sub>/AC Synthesized at 450 °C, 500 °C and 550 °C

Entry	Catalyst	d-Spacing (nm)	Crystallite size (nm)	Conversion (%)
1	CuCo <sub>0.2</sub> /AC-450	2.3170	32.0	86.0
2	CuCo <sub>0.2</sub> /AC-500	2.3174	27.9	10.5
3	CuCo <sub>0.2</sub> /AC-550	2.3188	24.4	6.8

\*Reaction conditions: 0.1 g catalyst, 2.6 ml benzyl alcohol, 3.3 ml H<sub>2</sub>O<sub>2</sub>, 20 ml toluene as solvent, T = 80 °C, t = 2 h.

the prepared catalysts is selective to benzaldehyde only. The bimetallic Cu and Co catalysts showed improvement compared to previous bimetallic catalysts using Cu and Ni which only oxidized benzyl alcohol to merely 48% [14], while in another study which combines Cu and Mn, showed slight increase with 63% conversion of benzyl alcohol [27]. Comparing these results with Cordoba *et al.*'s [28] results confirmed that cobalt-based solids have exhibited high catalytic activity due to the role of  $\text{Co}_3\text{O}_4$  nanoparticles acting as Lewis acid sites.

The benzyl alcohol conversion of above 70% was obtained at 80 °C for all  $\text{CuCo}_x/\text{AC}$  catalysts. At the present working temperature of 80 °C, it is expected that  $\text{H}_2\text{O}_2$  releases oxygen by decomposition. Chaudhari *et al.* reported that  $\text{H}_2\text{O}_2$  is more effectively consumed for the oxidation of benzyl alcohol at higher temperatures [29]. However, the temperature should not be too high as it will lead to self-decomposition of  $\text{H}_2\text{O}_2$  inefficiently [30]. Moreover, the evaporation of solvent at higher temperatures may also result in reduced conversion of benzyl alcohol.

Deposition-precipitation method in liquid medium uses precipitation process to bring Cu and Co together while the deposition process enables depositing these active sites onto the AC support surface. The activity of  $\text{CuCo}_x/\text{AC}$  catalysts was found to be very dependent to the composition. Table 1 compares the catalytic performances of  $\text{CuCo}_x/\text{AC}$  catalysts with different Co loadings. The benzyl alcohol conversion increased with increasing Co content until 0.2 mol under the same Cu loading. The highest activity (Table 2, Entry 4) was achieved for  $\text{CuCo}_{0.2}/\text{AC}$  catalysts at 86% conversion. As the amount of Co increased to 0.5 and 1.0 mol, the catalytic activity decreased. The activity dependence on the Co content in  $\text{CuCo}_x/\text{AC}$  catalysts demonstrated that increasing the Co content from 0.2 mol to 0.5 and 1.0 mol will block the accessibility of Cu active sites thus decreasing the catalytic activity. Such phenomena were also observed for Au-Cu/ $\text{TiO}_2$ -nanobelt catalysts whereby too much  $\text{CuO}_x$  reduced the accessibility of reactive molecules for the Au active sites [13]. It is worth to note that, although as the amount of Co increased to 0.5 and 1.0 mol, the catalytic activity decreased, the conversion of benzyl alcohol were still higher compared to single metal catalyst, Cu/AC and Co/AC.

As demonstrated from changes in crystal structure, the

combined  $\text{CuCo}_x$  addition onto AC support enhanced the catalytic activity of the samples due the synergistic effect of Cu and Co species. These results suggested that the addition of a second metal dopant increased the number of the active sites on the porous AC support that are available for the oxidation reaction, resulting in enhanced catalytic activity compared to their monometallic counterparts. The presence of  $\text{Co}_3\text{O}_4$  with  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  active sites contributes to the redox property due to the ability of  $\text{Co}^{3+}$  to be reduced to  $\text{Co}^{2+}$  [31]. A synergistic effect on the conversion of benzyl alcohol over  $\text{Co}_3\text{O}_4$  supported on activated carbon was reported, indicating that the activated carbon provided sites for dioxygen adsorption and activation, whereas  $\text{Co}_3\text{O}_4$  catalyzes the dehydrogenation reaction [32].

$\text{CuCo}_{0.2}/\text{AC}$  sample had the highest crystallinity among the samples, an increase in the cobalt loading from 0.2 mol to 0.5 and 1.0 mol lead to decreasing the catalytic activity. The number of active sites is attributed to the composition of the surface due to the presence of metal ions and the crystallinity [33]. The high crystallinity is deduced to improve the catalytic activity due to favourable charge transport properties [34]. When Co loading was above the optimum value (0.2 mol), the crystallinity of the samples decreased, thereby decreasing the catalytic activity. Furthermore, the agglomeration of excess Co loading could act as recombination sites that deter the smooth transfer of electrons [35] thus reducing the catalytic activity. The  $\text{CuCo}_{0.2}/\text{AC}$  samples obtained at 500 °C and 550 °C displayed a lower catalytic activity compared to  $\text{CuCo}_{0.2}/\text{AC}$  prepared at 450 °C as shown in Table 2. The  $\text{CuCo}_x/\text{AC}$  samples obtained at temperatures higher than 450 °C showed a decreased catalytic activity possibly owing to the lower crystallinity of the samples. The crystallite sizes of  $\text{CuCo}_x/\text{AC}$  also decreased by increasing the calcination temperature. The results clearly indicated that the growth and crystallization of  $\text{CuCo}_x/\text{AC}$  had been greatly influenced by the temperature.

## CONCLUSIONS

The CuCo bimetallic catalysts with different Co loadings were successfully deposited on activated carbon (AC) using a very facile deposition-precipitation method. Based on the results, the amount of Co loading and different



calcinations temperatures only influence the crystallinity of the samples without changing the morphology and particle size. The catalysts obtained were all active for the oxidation of benzyl alcohol to benzaldehyde under mild conditions. The addition of Co in the range of 0.1-1 mol exhibited the high catalytic activity above 70% conversion. The best synergistic effect of the CuCo interaction in comparison to their monometallic Cu/AC and Co/AC was observed for CuCo<sub>0.2</sub>/AC synthesized at 450 °C with 86% conversion of benzyl alcohol. The optimum cobalt amount at 0.2 mol contributes to the highest crystallinity of the catalyst obtained. Crystallinity has a crucial influence on the available active sites for the oxidation reaction. Thus, it was demonstrated that the catalytic properties can be tuned *via* controlling the ratio of Cu and Co at the optimum calcination temperature.

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