# PREPARATION OF BIMETALLIC Co-Cu SUPPORTED ON ACTIVATED CARBON CATALYST FOR SELECTIVE PRODUCTION OF 2,5-FURANDICARBOXYLIC ACID

● TRAN THI TUONG VI - LE TAN KHANH TRINH

**ABSTRACT:**

The utilization of renewable resources such as biomass has been of great interest to scholars in the field of green chemistry. In this study, commercial activated carbon was applied as catalyst support. The bimetallic catalyst was synthesized by the impregnation method with different ratios of cobalt to copper loading on the catalyst support. This catalyst has been used in the conversion of 5-hydroxymethylfurfural (5-HMF) by using hydrogen peroxide ($H_2O_2$) as liquid oxidant to form 2,5-furandicarboxylic acid (2,5-FDCA) through an oxidation process. Various reaction parameters such as reaction time (h), reaction temperature ($^0C$), and catalyst loading (wt.%) on the catalytic performance were investigated. The optimal catalyst was prepared using cobalt and copper in a mass ratio of 4:1, giving high HMF conversion (greater than 99%) and 40% of FDCA selectivity at $110^0C$ for 5 hours.

**Keywords:** bimetallic catalyst, bio-based-polymer, carbon catalyst, 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, oxidation.

## 1. Introduction

5-Hydroxymethylfurfural (HMF), which is a renewable resource of lignocellulosic biomass conversion, derived from cellulose through isomerization/dehydration of hexoses. 5-HMF has drawn attention from scientists and has become a significant and valuable platform chemical in bio-based green chemistry. Its derivatives including 2,5-furfuryldiamine, levulinic acid and 2,5-furandicarboxylic acid (2,5-FDCA) are suitable as starting materials for polymeric materials synthesis such as polyamides, polyesters and polyurethanes. In 2004, the US Department of Energy identified FDCA as one of the twelve priority chemicals for establishing the "green" chemistry industry of the future [1]. 2,5-FDCA can be applied in many fields to be useful in organic synthesis, pharmacology, and metal-organic framework. However, the use as a precursor monomer to synthesis polymer building block for the production of polyethylene terephthalate (PET) is the most important application of this product due to the similar structure with terephthalic acid which can be obtained from fossil resources [1-3]. In previous works, 2,5-FDCA have been synthesized by oxidation of HMF via homogeneous metals salts catalysts ($KMnO_4$, $CuCl_2$, $Co^{2+}/Mn^{2+}/Br$, etc.). However, there appear to have some drawbacks such as long reaction time, high cost, large waste amount of toxic chemicals, difficulty in catalyst

recycling and environmental destruction [1, 4]. Different kinds of heterogeneous catalysts have been developed, focusing on noble metal-supported heterogeneous catalysts, such as platinum (Pt), gold (Au), ruthenium (Ru) and palladium (Pd). These kinds of heterogenous catalysts have shown a good catalytic activity, reusability and stability but their high cost still remains as a downside. For this reason, low-cost catalysts which included nonnoble metallic (Cu, Ni, Co, Fe) on modified support have become a promising substitute to solve the before mentioned disadvantage of high cost. Currently, the bimetallic catalyst has been considered as a potential oxidative catalyst. Many researchers have expressed their interest and conducted studies on bimetallic and non-noble metal and developed this catalyst in the oxidation process.

In this work, the author focuses on using Co-Cu bimetallic catalyst supported on commercial activated carbon (Co-Cu/CAC) for 5-HMF oxidation to produce a chemical building block (2,5-FDCA). This catalyst with the mesoporous structure decreases the accumulation of polar compounds on the catalyst surface and increases the hydrophobicity surface to enhance the active site of the catalyst.

## 2. Materials and methods

### 2.1. Materials

All reagents were analytical grade and without further purification. Cobalt nitrate (99%), Copper nitrate (99%), commercial activated carbon, Sodium carbonate, Ethanol (99%), hydrogen peroxide 30% were obtained from Xilong Scientific Co., Ltd. (Shanghai, China). Commercial activated carbon was collected from Viet Nam. 2,5-Furandicarboxlic acid, 5-Hydroxymethylfurfural were purchased from Sigma-Aldrich (USA).

### 2.2. Preparation of xCo-Cu/CAC catalyst

Co-Cu bimetallic are loaded on CAC (commercial activated carbon) by using wet-impregnation method. The xCo-Cu/CAC catalyst with different metal compositions of Co-Cu mass ratio (x: 1 - 4) was prepared respectively. In this step, the nitrate salts $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ was mixed with deionized water (DI) in round bottom flask under stirring to dissolve the precursors completely. After that, the CAC was slowly added in precursor solutions. Next, the slurry is stirred at $40^0C$ until water had evaporated. Then the solution was dried at $80^0C$ overnight. The solid powder obtained is reduced under a flowing $H_2$ at $450^0C$ for 2 hours at heating of $5^0C/min$. In this part, the catalyst with different metal compositions of Co-Cu mass ratio from 1 to 4 was obtained.

The porous structure, surface area and pore size were determined by $N_2$ sorption isotherm. The surface area was calculated by using Brunauer Emmett Teller (BET). The pore size, pore volume was derived from Barrett-Joiner-Halender model (BJH). The physical structure characteristic and surface morphology of the catalyst were studied by X-ray diffraction (XRD). The inorganic contents of catalyst were determined by X-ray fluorescence (XRF) and identified the elements that exist within catalyst (elemental composition or oxidation state of Co/Cu).

### 2.3. 2,5-FDCA production from 5-HMF oxidation

Firstly, 0.1 g HMF and 0.125 g $Na_2CO_3$ were dissolved in 36 mL DI water and transferred in the Teflon-lined stainless steel autoclave reactor. Then 0.01g Co-Cu/AC catalysts are added to this solution. After that, the amount of $H_2O_2(aq)$ was added to the solution drop wisely. After being finished, the reactor was put into ice water for rapid cooling to room temperature. Finally, the content of HMF and its derivatives in samples were analyzed by high-performance liquid chromatography (HPLC) with a PDA detector on the Eclipse Plus C18 column (250 mm × 4.6 mm). The obtained products were compared with the known commercially pure samples.

The 2,5-FDCA yield, 2,5-FDCA selectivity and HMF conversion were calculated by Equation 1, 2 and 3, respectively [5].

$$\text{FDCA yield (\%)} = \frac{C_{FDCA\,product\,(ppm)}}{C_{HMF\,started\,(ppm)}} \times 100 \quad (1)$$

$$\text{FDCA selectivity (\%)} = \frac{\text{Yield}}{\text{Conversion}} \times 100$$
$$= \frac{C_{FDCA\,product\,(ppm)}}{C_{HMF\,reacted\,(ppm)}} \times 100 \quad (2)$$

$$\text{HMF selectivity (\%)} = \frac{C_{HMF\,reacted\,(ppm)}}{C_{HMF\,started\,(ppm)}} \times 100 \quad (3)$$

## 3. Results and discussion

### 3.1. Characterization of xCo-Cu/CAC catalyst

Representative $N_2$-sorption and XRD spectra of 4Co-Cu/CAC catalyst are shown in Fig. 1. $N_2$ adsorption-desorption isotherms have been conducted and a typical isotherm for 4Co-Cu/CAC catalyst was given in Fig. 1 (a). There is a characteristic of shape and isotherm type IV indicating mesoporous structure (according to IUPAC classification) with a hysteresis loop of type H4 corresponded to a narrow-slit pore, particles with internal voids of regular shape and broad size distribution and disordered structure. The details of the Brunauer-Emmett-Teller (BET) specific surface area, pore volume and average pore diameter are summarized in Table 1. The 4Co-Cu/CAC catalyst presented a large surface area ($S_{BET}$ = 494.12 $m^2g^{-1}$) and pore size (3.06 nm).

Fig. 1 (b) shows the XRD patterns of the catalysts. From the figure, the presence of Co and Cu on CAC was also confirmed. The diffraction of Co and Cu loaded on CAC demonstrated at three peaks of Co ($2\theta$ of $44.20^0$, $51.50^0$, and $75.90^0$) and Cu ($2\theta$ of $43.50^0$, $50.60^0$ and $74.40^0$) indicating that Co and Cu were reduced under reduction condition which can validate to the single face center cubic (FCC) structure of bimetallic nanoparticles structure [6-8]. However, the presence of CuO and $Co_3O_4$ at $2\theta$ of $35.70^0$ and $38.87^0$, respectively due to unreduced catalyst or oxidation of metals under atmosphere [9, 10].

Results of elemental analysis of catalyst by X-ray fluorescence (XRF) were shown in Table 1. This results presences the content elemental of catalyst after reduction. As shown in Table, the % Co and % Cu was 73.90%, 26.10% respectively at 4Co-Cu/CAC catalyst.

### 3.2. Oxidation of HMF

The effects of catalytic activity and selectivity on HMF conversion at different mass ratios of Co-Cu on the catalyst are shown in Fig. 2. The HMF conversion was given nearly 100 % it is demonstrated that the Co-Cu could enhance the

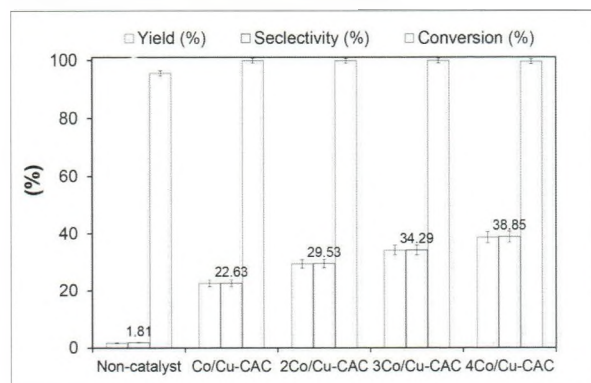**Figure 1: Representative (a) $N_2$-sorption and (b) XRD spectra of 4Co-Cu/CAC catalyst**
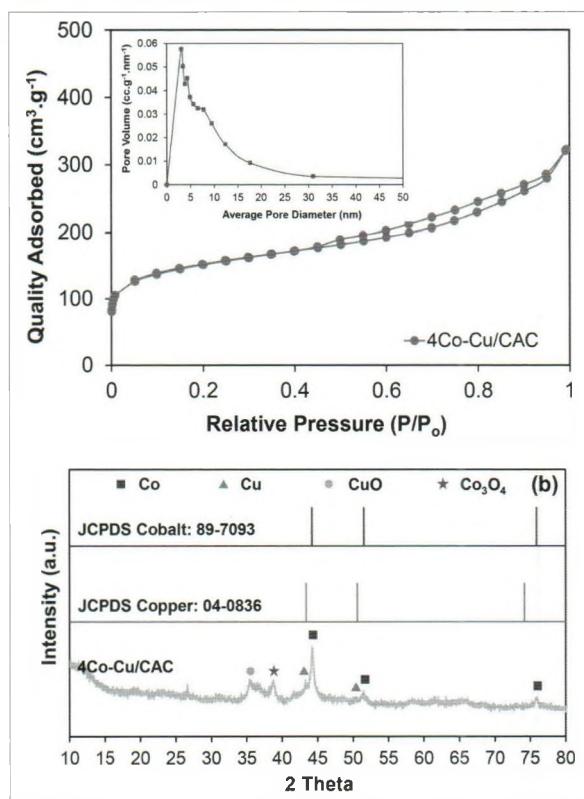


reaction rate and diffusion of reactant to the catalyst sites. Moreover, $H_2O_2$ is a rich $O_2$ sources support [5]. Besides, the yield and selectivity of 2,5-FDCA increased with increasing the mass ratio Co-Cu from 22.63% to 38.85%. The 4Co-Cu/CAC catalyst was shown the best activity catalyst with nearly 100% HMF conversion and 40% 2,5-FDCA yield and selectivity. Besides that, the HMF oxidation carried out without catalyst at $110^0C$ for 5 h was investigated. The HMF conversion was reached 95.59% but the 2,5-FDCA selectivity was low (1.81%) since cleaved the furan ring, resulting in undesired/unwanted products [11]. Scheme 1 shows the reaction pathway of HMF oxidation to produce FDCA. [1, 12]. Therefore, the mesoporous structure and bimetallic Co-Cu catalyst could enhance the reaction rate and select on 2,5-FDCA.

**Table 1. Physical and chemical properties of the 4Co-Cu/CAC catalysts**

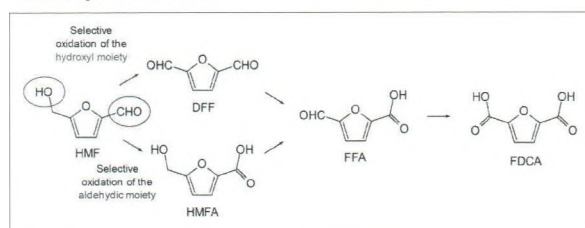| Sample | BET surface area (m²/g) | Pore size (nm) | Pore volume (cm³/g) | | XRF | |
|---|---|---|---|---|---|---|
| | | | Total pore | Micropore | % Co | % Cu |
| 4Co-Cu/AC | 494.12 | 3.06 | 0.30 | 0.12 | 73.90 | 26.10 |

**Figure 2:** *Catalytic activity of HMF oxidation at 110ºC for 5 h, 10 wt.% of catalyst loading under different xCo-Cu/CAC catalyst*



**Scheme 1:** *HMF oxidation to produce FDCA production*



were presented large surface area up to 494 $m^2/g$. The xCo-Cu/CAC catalyst contained the mesopore structure. Besides that, XRD and XRF have demonstrated the structure and content Cu, Co of catalyst after reduction catalyst. The bimetallic catalyst was discovered to be an important factor for enhanced the 2,5-FDCA selectivity. The highest 2,5-FDCA yield, 2,5-FDCA selectivity, and HMF conversion at optimized conditions were 38.64 %, 38.85%, 99.50%, respectively ∎

### 4. Conclusions

The xCo-Cu/CAC catalyst could be prepared by impregnation method with different mass ratios between Co and Cu. The 4Co-Cu/CAC catalysts

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# NGHIÊN CỨU ĐIỀU CHẾ XÚC TÁC KIM LOẠI Co-Cu TRÊN CHẤT MANG CARBON HOẠT TÍNH CHO QUÁ TRÌNH SẢN XUẤT AXIT 2,5-FURANDICARBOXYLIC

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**TÓM TẮT:**

Việc sử dụng các nguồn tài nguyên tái tạo như sinh khối đã và đang được các nhà nghiên cứu khoa học quan tâm. Trong nghiên cứu này, than hoạt tính thương mại đã được sử dụng làm chất mang. Chất xúc tác lưỡng kim được tổng hợp thông qua phương pháp ngâm tẩm với các tỷ lệ khác nhau giữa cobalt và đồng trên nền chất mang. Và được ứng dụng làm chất xúc tác cho quá trình chuyển hóa 5-hydroxymethylfurfural (5-HMF) để tạo thành axit 2,5-furandicarboxylic (2,5-FDCA) với hydro peroxit (H₂O₂) là chất oxi hóa cho quá trình phản ứng. Các thông số phản ứng khác nhau như thời gian phản ứng (h), nhiệt độ phản ứng (⁰C) và tải trọng chất xúc tác (% wt.) trên hiệu suất xúc tác đã được khảo sát. Chất xúc tác tối ưu được điều chế với tỷ lệ khối lượng 4:1 giữa cobalt và đồng cho kết quả chuyển hóa HMF cao (> 99%) với 40% hiệu suất và độ chọn lọc của FDCA tại 110⁰C trong 5 giờ.

**Từ khóa:** Xúc tác lưỡng kim, polyme sinh học, xúc tác carbon, 5-hydroxymethylfurfural, axit 2,5-furandicarboxylic, quá trình oxi hóa.