Green synthesis of copper nanoparticles using *Cocoa* pod extract and its catalytic activity in deep oxidation of aromatic hydrocarbons

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Abstract

An effective and green technique was performed for the synthesis of copper nanoparticles (CuNPs) from an organic resource using the *Cocoa* pod (CCP) extract as a reducing agent. The formation of CuNPs was confirmed by ultraviolet–visible absorption spectroscopy (UV–Vis) at the wavelength range of 500–600 nm. The optimized conditions for the synthesis of CuNPs using CCP extract as a reducing agent were determined by the volume ratio of $\text{Cu}(\text{NO}_3)_2$ solution/CCP extract of 3.5/1.5, stirring rate of 300 rpm, pH solution of 7.5, the temperature of 75 °C and the synthesis duration within 180 min. At these conditions, the X-ray diffraction result revealed a face-centered cubic structure of zero-valent copper with a highly crystalline and an average size of 34.4 nm. Fourier transform infrared spectroscopy result confirmed the presence of flavonoids, polyphenolic, and alkaloids components in CCP extract which can act as the reducing and stabilizing agents for CuNPs formation. At the optimized synthetic conditions, CuNPs loaded on various supports (Al_2O_3 , CeO_2 , and TiO_2) were prepared following the same protocol and then applied for catalytic deep oxidation of aromatic hydrocarbons (AHs). Among them, CeO_2 was the best support in AHs deep oxidation, and the sample of 7.5Cu–Ce (7.5 wt% of CuNPs supported on CeO_2) was the most efficient. Compared with 5Cu–Ce and 10Cu–Ce, the 7.5Cu–Ce sample exhibited a higher benzene conversion at a low temperature (275–325 °C) and reached the full conversions of benzene, toluene, ethylbenzene, and xylene (BTEX) to carbon dioxide and water vapor below 450 °C. Furthermore, the 7.5Cu–Ce sample showed great stability for such reactions at 300 °C as proven by the unchanged conversions of BTEX during 48 h.

Keywords Green synthesis · Copper nanoparticles · *Cocoa* pod · Deep oxidation · Aromatic hydrocarbons

1 Introduction

Volatile organic compounds (VOCs) in the atmosphere have been known as a source of contaminants that adversely affect air quality and human health [5, 22]. VOCs have been found to be the major contributing factor to ozone layer depletion, which leads to global warming. With respect to human health, exposure to VOCs

may cause respiratory and cardiovascular disease and even devotes to cancer [5, 11]. Among sources of VOCs spreading, irrespective of natural causes, petroleum refining and petrochemical plants take account for the majority. According to the report from Li et al., benzene, toluene, and acetone were the most abundant emission species from coke production [19]. Zhang et al. measured the emission characteristics of VOCs in different

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areas of a petroleum refinery, showing more than 50% of the total VOCs emitted from the refining area, including 2-methylpentane, 2,3-dimethylbutane, methylcyclopentane, 3-methylhexane, and butane [39]. Chen et al. found out that the naptha-cracking region mainly produced propene, 1, 3-butadiene, benzene, isobutene, and butane while butane, isobutene, and benzene were the major outputs in the aromatic region [6]. Recently, aromatic hydrocarbons are of the most concern due to their variety, abundance, and toxicity. In fact, benzene, toluene, ethylbenzene, xylene (BTEX) mostly found in natural gas and oil deposits, or in petroleum refining and petrochemical plants [31, 35] have harmful impacts on human health. When exposed to more than 100 ppm of benzene (considered as the exposure limit), irritation to eye, nose, and throat, chest tightening, or more serious health symptoms can occur [33].

Catalytic deep oxidation stands out as a practical technology, permitting to effectively remove VOCs in both gaseous and aqueous phase, even at low concentration [13, 38], mainly based on catalysts. The catalytic oxidation is promising in the reduction of emissions because it is able to remove the emissions from high to very low levels, which may meet the needs of more stringent emission control in future. Also, compared with thermal incineration processes, the operating temperature of the catalytic oxidation is much lower. This is helpful for avoiding the formation of toxic byproducts and for reducing energy consumption.

More recently, great attention has been paid to copper nanoparticles (CuNPs) thanks to their excellent catalytic performances in VOCs oxidation [17–18, 28]. Various methods for the synthesis of CuNPs have been developed, mainly based on the chemical reduction of metal salts or complexes [15, 30]. In particular, the plant extracts acting as the reducing agents have been introduced to the bio-synthesis of metal nanoparticles, thanks to their low-cost and non-toxic features. *Cocoa*—originating wildly in the tropical forests of Central and South America was introduced to Southeast Asia and Vietnam for a long time. The *cocoa* pods as the by-product of the *cocoa* processing (accounting for 52–76 wt% of the total fruit) are often discarded due to its low market value. *Cocoa* pods contain many compounds such as gallic acid, alanine, glutamic acid, flavonoids, polyphenols, etc. [8], acting as reducing agents for the synthesis of highly efficient CuNPs [14, 21]. The *cocoa* extract has also been used as a reducing and stabilizing agent in the biosynthesis of silver [16] and Pd/CuO [24] nanoparticles. However, to the best of our knowledge, *Cocoa* pod extract (CCP extract) has never been reported as reducing and stabilizing agents for the synthesis of CuNPs.

In this paper, CuNPs and CuNPs loaded on various supports (Al_2O_3 , CeO_2 , and TiO_2) were synthesized from $\text{Cu}(\text{NO}_3)_2$ solution using CCP extract as a reducing agent. The starch was used during synthesis as a stabilizing agent, leading to monodispersed Cu nanoparticles in an aqueous medium as well as stabilizes the Cu nanoparticles from air oxidation. The effects of the synthesis duration, the volume ratio of $\text{Cu}(\text{NO}_3)_2$ solution/CCP extract, the stirring rate, pH solution, and the reaction temperature were assessed. The physico-chemical properties of the obtained CuNPs were investigated. Their catalytic activities were investigated in deep oxidation of aromatic hydrocarbons (AHs) including benzene, toluene, ethylbenzene, and xylene in the gaseous phase.

2 Experimental

2.1 Materials

Cocoa pods were collected from Tien Giang province, Vietnam. After washing and draining, 50 grs of the *Cocoa* pods were minced and mixed with 1000 mL of deionized water. Then, the mixture is heated to 80 °C for 2 h under stirring. Finally, the *Cocoa* pod extract (CCP extract) was filtered and preserved at 4 °C for the further experiments. Copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, > 99.8%), starch ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$, > 99%) and sodium hydroxide (NaOH , > 99.9%) were purchased from Merck.

2.2 Preparation of CuNPs and supported-CuNPs

The green synthesis of CuNPs was performed by adding 1.5 grs starch to the aqueous solution of 0.02 M $\text{Cu}(\text{NO}_3)_2$ with vigorous stirring, leading to the color change from blue to white. Afterward, CCP extract was added to the mixture and the color transformation from white to blue moss occurred in the aqueous phase. NaOH solution (0.1 M) was added to the reaction mixture under continuous vigorous stirring (200–400 rpm) to adjust the pH (8.5–9.5) and then heated to the desired temperature (70–80 °C). The formation of the CuNPs is confirmed by the color change from green to brown. The effects of the reaction factors involving the time, volume ratio of $\text{Cu}(\text{NO}_3)_2$ solution/CCP extract, stirring rate, pH, and temperature on the CuNPs formation were investigated.

CuNPs loaded on various pre-formed supports (Al_2O_3 , CeO_2 , and TiO_2) were in-situ synthesized at the optimized conditions following the same protocol.

2.3 Characterization methodology

The formation of CuNPs in solution was observed by UV–Vis spectrophotometer (UV–1800, Shimadzu) at a scanning speed of 200–800 nm with a resolution of 1 nm. X-ray powder diffraction (XRD) patterns were collected on Bruker D2 Phaser diffractometer using CuK α radiation ($\lambda=0.154$ nm) in $2\theta=10\text{--}80^\circ$ with the scanning step of 0.02° . The average crystal size of CuNPs, d (nm), was calculated according to the Scherrer equation [26]:

$$d(\text{nm}) = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K , the Scherrer constant, is taken to be 0.94, λ is the wavelength of the X-ray, β is the line width at half maximum height of the peak in radians, and θ is the position of the peak in radians. The morphology of samples was characterized by scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) on JST-IT 200 instrument. The morphology, particle size, and crystal phases were also estimated by HRTEM analysis on JEOL 2100F instrument. The CCP extract and the surface of obtained materials were detected by Fourier transform infrared spectroscopy (FT-IR) carried out on a Tensor 27-Bruker spectrophotometer operating in the range of $400\text{--}4000\text{ cm}^{-1}$ at a resolution of 2 cm^{-1} .

2.4 Catalytic activity in deep oxidation

The catalytic activity of supported-CuNPs was investigated by the AHs treatment and performed in a fixed tubular quartz reactor (inside diameter of 8 mm) under atmospheric pressure at a temperature range of $275\text{--}450^\circ\text{C}$. The weight hourly space velocity (WHSV) was $60,000\text{ mL h}^{-1}\text{ g}^{-1}$, and the mass of catalyst was 0.2 grs with a size range of $0.25\text{--}0.50\text{ mm}$. The inlet concentrations of AHs and oxygen in nitrogen were 0.34 and 10.5 mol%, respectively. The reactant and product mixtures were analyzed with an Agilent 6890 Plus Gas Chromatograph with FID detector and capillary column DB-624 (Oven temperature program: isothermal analysis at 150°C ; detector temperature: 300°C ; injector temperature: 250°C ; carrier gas: nitrogen; inlet pressure: 20 PSI) and with a TCD detector and capillary column TG-BONQ (Oven temperature program: 50°C (5 min) $\rightarrow 10^\circ\text{C}/\text{min} \rightarrow 150^\circ\text{C}$ (5 min); detector temperature: 180°C ; injector temperature: 180°C ; carrier gas: helium; inlet pressure: 5 PSI). The tests were conducted in triplicate to ensure the accuracy of the results. The AHs conversion was calculated as follows:

$$X_{\text{AHs}}(\%) = \frac{[\text{AHs}]_{\text{in}} - [\text{AHs}]_{\text{out}}}{[\text{AHs}]_{\text{in}}} \times 100\% \quad (2)$$

where $X_{\text{AHs}}(\%)$ —AHs conversion; $[\text{AHs}]_{\text{in}}$ and $[\text{AHs}]_{\text{out}}$ —the input and output quantities of AHs, respectively.

The most outstanding catalyst was selected for the catalytic stability in the AHs oxidation. The reaction was carried out at 300°C for 48 h and the conversions of AHs were recorded every 2 h.

3 Results and discussions

3.1 Green synthesis of copper nanoparticles

The formation of CuNPs was monitored by UV–Vis spectroscopy as shown in Fig. 1. The effect of synthesis duration (see in Fig. 1a) showed that the CuNPs formation takes place at 80°C for at least 60 min. The broad peak was observed at a range of $500\text{--}600\text{ nm}$, indicating the formation of CuNPs in the solution. The formation of the CuNPs was also confirmed by the color change from green to brown Fig. 2. Upon the reaction time, the absorbance intensity increased, evidencing the higher conversion of Cu^{2+} ions to Cu^0 nanoparticles (CuNPs). The maximum signal intensity attributed to surface plasmon resonance of zero-valent CuNPs was observed at 180 min and 210 min, confirming the full reduction of Cu^{2+} to Cu^0 . Therefore, the time of 180 min was chosen for the further characterizations. With the volume ratio of $\text{Cu}(\text{NO}_3)_2$ solution/CCP extract of 3.5/1.5, CuNPs were obtained at the highest performance (see in Fig. 1b). The components in the extract with high concentrations could effectively reduce the Cu^{2+} ions to Cu^0 , and also act as capping agents to stabilize CuNPs through steric hindrance, thus preventing their aggregation [29]. Figure 1c showed the concentration of the obtained CuNPs increased when the stirring rate increased from 200 to 300 rpm, but slightly dropped applying 400 rpm. Due to the increase of nanostructure concentration, stronger mixing was essential to provide uniform heat and mass transfer [27]. Besides, CuNPs were detected at the highest absorbance by the UV–Vis spectra at pH 8.5 (see in Fig. 1d) and at the temperature of 75°C (see in Fig. 1e).

From the obtained results, the optimized conditions for the synthesis of CuNPs using C.C extract as a reducing agent were determined involving the volume ratio of $\text{Cu}(\text{NO}_3)_2$ solution/C.C Extract of 3.5/1.5, stirring rate of 300 rpm, pH 7.5, the temperature of 75°C and the synthesis duration of 180 min.

X-ray diffraction analysis (XRD) of CuNPs was shown in Fig. 3a. Three Bragg reflections with $2\theta=43.6^\circ$, 50.7° , and 74.4° were recorded corresponding to (111), (200) and (220) lattice planes, which are characteristics of the face-centered cubic structure of zero-valent copper (JCPDS card No. 04–0836). Besides, a broad diffraction peak at

Fig. 1 UV-Vis spectra of CuNPs solutions under various conditions; **a** Effect of synthesis duration, **b** Effect of $V_{\text{Cu}^{2+}}/V_{\text{Ext}}$ volume ratio, **c** Effect of stirring rate, **d** Effect of pH solution, and **e** Effect of synthesis temperature

$2\theta = 36.2^\circ$ of the cuprite ($\bar{1}\bar{1}1$) plane was also observed [27]. Therefore, XRD analysis confirmed the presence of pure CuNPs with a highly crystalline structure. The average crystal size of the CuNPs can be calculated by the Debye–Scherrer equation with $K = 0.94$ at $2\theta = 43.6^\circ$, showing the value of 34.4 nm. Lattice parameter was determined through interplanar spacing (d-spacing) of the (111) planes at $2\theta = 43.6^\circ$, as follows:

$$\alpha = d\sqrt{h^2 + k^2 + l^2} \quad (3)$$

where “ α ” is a lattice parameter [$\text{\AA}$], d is d-spacing [$\text{\AA}$]; and h , k , and l are the Miller indices of the (111) plane of the crystal. A d-spacing value of 2.075 $\text{\AA}$ with a lattice parameter of 3.594 $\text{\AA}$ for the Miller indices corresponding to (111) plane that matches well with standard lattice parameter ($\alpha = 3.615 \text{ \AA}$) [7].

Fig. 2 The color changes during the synthesis of CuNPs at various synthesis duration

Fig. 3 XRD diffraction pattern of CuNPs (a) and FT-IR spectra of CCP extract and CuNPs synthesized at the optimized conditions (b)

FT-IR spectra of CCP extract, CuNPs solution, and CuNPs powder were described in Fig. 3b. For the extracted sample, FT-IR analysis is used to detect the possible bioactive molecules, which are mainly responsible for the reduction of the Cu²⁺ ions to CuNPs. FT-IR spectrum manifested the strong peaks at 3295, 2850, and 1640 cm⁻¹, associated with the N–H bond of amines [1, 9], the C–H stretching, and the C=C stretch of alkenes or C=O stretch of amides [1], respectively. These characterized bands affirmed the presence of proteins and phenolic compounds in the extract which play the roles of the reducing and stabilizing agents. There are insignificant differences between

the CCP extract and CuNPs solution, probably because the compounds of CCP extract overlapped the peaks of CuNPs surface. However, the FT-IR spectrum of CuNPs solution showed the presence of a weaker signal compared to CCP extract, proving the functional groups contained the extract reacted to form CuNPs, so the concentration of the extract was significantly reduced. On the FT-IR spectrum of CuNPs powder, a band centered at 2285 cm⁻¹ was related to the Cu–H stretching [34], and the peaks at 640 and 530 cm⁻¹ corresponded to Cu–O bond were not detected, indicating the formation of only CuNPs. From the analysis of FT-IR studies, we confirmed that the proteins and

phenolics compounds in CCP extract possibly performed the dual functions for the formation of CuNPs.

In order to study the morphology and size of the bio-synthesized CuNPs, the SEM image was shown in Fig. 4a. The result exhibited the presence of nanosized spherical particles (in the range of 20–50 nm) with a uniform particle shape, in agreement with the crystal size of CuNPs calculated from XRD pattern. HRTEM has been employed to characterize the shape, size, and morphology of the CuNPs sample. The HRTEM analysis proved the formation of nanocrystalline copper particles with spherical shape and the size was estimated in a range of 30–40 nm (seen in Fig. 4b). The inset in Fig. 4b demonstrated that the CuNPs had both the (111) and (200) planes of structured CuNPs with the d-spacings of 0.22 and 0.24 nm, respectively. The results were consistent with the XRD analysis as mentioned above.

The elemental compositions of the bio-synthesized nanoparticles were determined by EDS analysis. The EDS spectrum of CuNPs synthesized at the optimized conditions is shown in Fig. 5. It shows high intense major peaks of elemental Cu with an atomic percentage of 75.77%, which was typical for the absorption of metallic copper because of surface plasmon resonance. The appearance of weak signals of O (12.53%) and C (11.70%) together with strong metallic copper peak may be owing to the presence of bio-molecules that are bound to the surface of CuNPs.

3.2 Characteristics and performance of CuNPs loaded on various supports in deep oxidation of benzene

X-ray diffraction analyses (XRD) of the CuNPs samples loaded on various supports with the CuNPs content fixed

Fig. 5 EDS spectrum of CuNPs synthesized at the optimized conditions

at 5 wt% were shown in Fig. 6. The crystal phases of copper (Cu^0) also appeared at $2\theta = 43.6^\circ$, 50.7° , and 74.4° on 5Cu–Al, 5Cu–Ce, and 5Cu–Ti samples, indicating the successful synthesis of CuNPs on such supports. The average crystal sizes of the CuNPs loaded on Al_2O_3 , CeO_2 , and TiO_2 were determined as 31.5, 26.5, and 27.2 nm, respectively. It proves that the formation of CuNPs on the support surface helped to prevent the agglomeration of CuNPs, leading to reducing the size of CuNPs. In which, CuNPs with the smallest particle size were detected on 5Cu–Ce samples, demonstrating the positive influences of CeO_2 support for the dispersion of CuNPs. SEM images of 5Cu–Al, 5Cu–Ce, and 5Cu–Ti samples showed the presence of nanosized particles (20–50 nm) with highly porous structures Fig. 7. However, a high level of agglomeration of CuNPs was

Fig. 4 SEM (a) and HRTEM (b) image of CuNPs synthesized at the optimized conditions

Fig. 6 XRD diffraction patterns of the samples; **a** Al_2O_3 , **b** CeO_2 , **c** TiO_2 , **d** CuNPs, **e** 5Cu-Al, **f** 5Cu-Ce, and **g** 5Cu-Ti

observed on the 5Cu-Al sample, being consistent with the results from XRD analyses.

Figure 8a presents the N_2 adsorption–desorption isotherms of 5C-Al, 5C-Ce, and 5C-Ti samples with the filled and open symbols indicating the adsorption and desorption values, respectively. The shapes of the adsorption isotherms for three samples obey type IV, which is associated with capillary condensation in the mesopores [4, 10, 40]. It clearly shows that less nitrogen was adsorbed on 5Cu-Al than those on 5Cu-Ce and 5Cu-Ti. Besides, the hysteresis loop of the 5C-Al sample did not exhibit the limiting adsorption at high P/P^0 values. This phenomenon is related to the presence of agglomerates, i.e., an assembly of particles rigidly joined together, in agreement with the SEM image of this sample. Figure 8b shows the specific surface areas of catalysts are arranged in the order: 5Cu-Al > 5Cu-Ti > 5Cu-Ce. However, the pore diameter and volume of catalysts are insignificantly different.

The catalytic performances of CuNPs, supported-CuNPs, and supports were evaluated in the deep oxidation of benzene as a function of the temperature, 275–450 °C shown

Fig. 7 SEM images of CuNPs loaded on various supports; **a** 5Cu-Al; **b** 5Cu-Ce; and **c** 5Cu-Ti

Fig. 8 N₂ adsorption/desorption isotherms **(a)** and the BET surface (S_{BET}), average pore diameter (d_{pore}), pore volume (V_{pore}) of CuNPs loaded on various supports **(b)**

Fig. 9 The catalytic activity of different samples in benzene oxidation

in Fig. 9. The benzene deep oxidation over the CuNPs fixed at 5 wt% on various supports prepared by the green synthesis is shown in Fig. 9a. It was found that the steep rise in benzene conversion was taken place with higher reaction temperatures. The catalytic activity of 5Cu-Ce sample was

much higher than those of CuNPs catalyst with the same content supported on TiO₂ and Al₂O₃ Fig. 9a, although its specific surface area is the smallest among three catalysts. Benzene conversion on 5Cu-Ce catalyst reached above 90% at 375 °C. Besides that, pure CeO₂ has a much higher

activity than TiO_2 and Al_2O_3 supports Fig. 9b. This can be explained that, in the catalytic process, CeO_2 serves as an oxygen supplier through either the formation of superoxide species (O^{2-}) by gas-phase oxygen reacting with oxygen vacancies on its surface or the direct involvement of lattice oxygen. Furthermore, the oxygen vacancies are easily formed in the CeO_2 support due to its high oxygen mobility to favor catalytic activity. The pure CuNPs sample was also relatively active in the benzene deep oxidation, reaching nearly 50% conversion of benzene at 450 °C. However, compared to the composite of CuNPs and CeO_2 (5Cu–Ce), the pure CuNPs and CeO_2 catalysts clearly showed much lower activities Fig. 9c.

It is well known that the Cu–Ce composite is one of the most important heterogeneous catalysts, widely used in catalytic oxidations [2–3, 20, 37], in particular the deep oxidation of benzene, toluene and xylene (Urbutis et al. 2014). Their high activity is attributed to the high oxygen storage capacity of ceria, the facile $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle, and the synergistic effect between Cu and CeO_2 [23].

3.3 Determination of the suitable CuNPs loaded on CeO_2 and its catalytic performance in deep oxidation of various aromatic hydrocarbons

XRD patterns of the CuNPs supported on CeO_2 (with different copper loadings) were displayed in Fig. 10. Clearly, the crystal phases of CuNPs also appeared on CuNPs– CeO_2 with various Cu contents, indicating the successful synthesis of CuNPs loaded on CeO_2 . The average crystal sizes of 5Cu–Ce, 7.5Cu–Ce, and 10Cu–Ce catalysts were 26.5, 27.3, and 29.6 nm, respectively Fig. 9. It could be explained that the crystallite size of the CuNPs slightly increased when increasing the contents of CuNPs loaded on CeO_2 .

Fig. 10 XRD diffraction patterns of the CuNPs supported on CeO_2 (circle: CeO_2 and diamond: Cu). a 5Cu–Ce, b 7.5Cu–Ce, and c 10Cu–Ce

support. The crystallite sizes of the CuNPs supported on CeO_2 samples were also smaller than that of the pure CuNPs. The comparison of BET specific surface area, average pore diameter, and pore volume are also exhibited in Fig. 11. The differences between 5Cu–Ce and 7.5Cu–Ce samples were negligible. Compared with 10Cu–Ce, the 7.5Cu–Ce catalyst had a higher BET surface area (40.9 vs. 28.5 $\text{m}^2 \text{g}^{-1}$), a larger pore volume (0.15 vs. 0.11 $\text{cm}^3 \text{g}^{-1}$) and larger pore diameter (10.3 vs. 9.2 $\text{cm}^3 \text{g}^{-1}$). Furthermore, 7.5Cu–Ce catalyst showed higher porous and smaller nanoparticles than 10Cu–Ce sample, leading to a better catalytic performance in BTEX deep oxidation.

HR-TEM analysis was performed to investigate the microstructural characteristics of 7.5Cu–Ce sample Fig. 12. The HR-TEM image confirmed the stability of CeO_2 nanorods after Cu addition. The CeO_2 nanorods were 20–30 nm in diameter and 100–200 nm in length. The inset below in Fig. 12 demonstrated that CeO_2 nanorods exposed both the (100) and (110) planes of structured fluorite CeO_2 with the d-spacings of 0.25 and 0.27 nm, respectively. Besides, the HR-TEM analysis also indicated that the formation of cubic particles of the CuNPs was exposed to CeO_2 nanorods. The estimated d-spacings of 0.25 and 0.29 nm (inset above Fig. 12) were assigned to the (111) and (200) crystal planes of CuNPs phase in 7.5Cu–Ce sample, respectively. The particle size of CuNPs has been estimated in the range of 30–40 nm. These analyses were entirely consistent with the corresponding XRD analysis.

The effect of CuNPs loading on the catalytic activity in benzene deep oxidation was investigated and shown in Fig. 13. The conversion of benzene was dramatically raised when reaction temperature increased from 275 to 360 °C and almost completed at 400 °C for all Cu–Ce

Fig. 11 The comparison of BET surface (S_{BET}), average pore diameter (d_{pore}), pore volume (V_{pore}) and the average diameter of CuNPs (d_{crys}) based on XRD results at $2\theta = 36.1^\circ$ of samples

Fig. 12 HR-TEM image of 7.5 wt% CuNPs sample loaded on CeO_2

Fig. 13 The catalytic activity in benzene oxidation of CuNPs loaded on CeO_2 with different copper contents

Fig. 14 The activity of 7.5Cu-Ce catalyst in deep oxidation of various aromatic hydrocarbons

catalysts. Their light-off temperatures (at 50% benzene conversion, T_{50}) on 5Cu-Ce, 7.5Cu-Ce, and 10Cu-Ce catalysts occurred at 310, 290, and 305 °C, respectively. Obviously, the 7.5Cu-Ce sample was the most efficient,

reaching a higher benzene conversion at a low temperature (275–325 °C). Therefore, the suitable CuNPs loading on CeO_2 was 7.5 wt%.

Fig. 15 The stability of 7.5Cu–Ce catalyst in deep oxidation of various aromatic hydrocarbons at 300 °C during 48 h (a) and XRD pattern of fresh and spent 7.5Cu–Ce catalysts (circle: CeO₂ and diamond Cu) (b)

The most efficient catalyst (7.5Cu–Ce) was further investigated in BTEX oxidation Fig. 14. The conversion of ethylbenzene was higher than those of benzene, toluene, and xylene. Evidently, the catalytic activity of all samples increased in the order: benzene < toluene < xylene < ethylbenzene. This consequence confirmed that the catalytic activity for the treatment of aromatic compounds highly relies on the strength of the weakest C–H bond in the structure, the ionization potential of methyl derivatives, and relative adsorption strength of model compounds [25, 32]. In which, the complete conversion of ethylbenzene took place at 350 °C; meanwhile, the temperatures for the complete conversions of xylene, toluene, and benzene were 400, 425, and 450 °C, respectively.

The 7.5Cu–Ce sample was selected to investigate the activity stability in AHs oxidation at 300 °C. The conversions of benzene, toluene, ethylbenzene, and xylene were unchanged for 48 h at 300 °C Fig. 15a, indicating the great stability of the 7.5Cu–Ce sample in such processes. It can be explained that the CeO₂ support with the advantage of redox property can be easily adjusted between reducing and oxidizing states that cause the donation and reception of oxygen, resulting in the oxidation of hydrocarbons at high temperatures. Besides, CeO₂ can also adsorb and desorb H₂O to generate the O^{•−} and OH^{•−} species, converting the hydrocarbons on catalyst surface into CO and CO₂ [41], and thus enhancing the stability of the 7.5Cu–Ce catalyst. The XRD result Fig. 15b of the spent catalysts (7.5Cu–Ce_S) showed that the phase composition of both samples was almost unchanged compared to the fresh one (7.5Cu–Ce_F). This proved that the structure of the catalyst was not damaged under reaction conditions at a temperature of 300 °C for 48 h.

4 Conclusion

The green synthesis of CuNPs and CuNPs loaded on various supports (Al₂O₃, CeO₂, and TiO₂) using *Cocoa* pod extract as a reducing agent proved to be an efficient and rapid approach towards BTEX deep oxidation. The catalyst characterizations confirmed the formation of highly crystalline sphere-shaped CuNPs with the size in a range of 20–50 nm. The formation of CuNPs on the support surface permitted to prevent the agglomeration of CuNPs and reduce their size, leading to enhancing their catalytic activity in BTEX deep oxidation. It was interesting to find out that the 7.5 wt% of CuNPs supported on CeO₂ exhibited the best catalytic performance towards BTEX deep oxidation. Hence, CuNPs and supported-CuNPs synthesized using plant-derived extracts (like *Cocoa-pods*) as reducing agents can be the promising approach in the development of catalytic systems for the aromatic hydrocarbons oxidation processes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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