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Facile Synthesis of Copper Nanocubes in Aqueous Phase for Catalytic Esterification Using Green-Conditions

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Abstract

This work demonstrated a simple and environmentally friendly method for synthesizing silica-supported copper nanocubes (CuNCs/SiO₂). The copper nanocubes, with a size of 15 ± 5 nm, were synthesized using green reagents and conditions. Ascorbic acid, water, and *di-n*-butyl sulfide were employed as reducing agent, solvent, and stabilizing ligand, respectively. The designed nanoscale catalyst was utilized for the esterification of acetic acid to methyl acetate at room temperature. The catalyst exhibited high efficiency, converting 80% of the reactant to the desired product (methyl acetate) after 24 hours of reaction at room temperature. The size and shape of copper nanocubes were characterized by transmission electron microscopy (TEM) and X-ray diffraction to characterize the formation of copper nanocubes, while the esterification product was characterized using gas chromatography-mass spectrometry.

Keywords: Copper nanocubes, Esterification, Green condition, Catalyst, Methyl acetate.

تحضير مركبات النحاس النانوية المكعبة واستخدامها في تفاعلات الاسترة باستخدام ظروف تفاعل و مواد صديقة للبيئة

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الخلاصة

تم تحضير مركبات النحاس النانوية المكعبة باستخدام طريقة صديقة للبيئة وتم تثبيتها على السيليكا. كانت المركبات المحضرة بحجم 15 ± 5 nm باستخدام مواد وظروف تفاعل صديقة للبيئة. تم استخدام اسكوربيك اسيد، الماء، كبريت ثنائي البيوتيل في التفاعل كعامل مختزل و مذيب ومادة مثبتة على التوالي. تم استخدام المادة النانوية كعامل مساعد في استرة حامض الخليك الى مثيل اسيتيت في درجة حرارة الغرفة. كان العامل المساعد النانوي فعال بحيث ان 80% من المتفاعلات تم تحويلها الى المادة الناتجة المتوقعة (خلات المثيل) بعد 24 ساعة تفاعل وفي درجة حرارة الغرفة. استخدمت تقنيات المجهر الالكتروني النافذ وفحص حيود الاشعة

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السينية لتشخيص حجم وشكل مركبات النحاس النانوية بينما استخدم جهاز كروماتوغرافيا الغاز لتشخيص نواتج تفاعل الاسترة.

1. Introduction

Anisotropic nanomaterials have garnered considerable attention in the 21st century due to their outstanding properties [1]. These nanomaterials have emerged as active catalysts in various chemical reactions owing to their distinctive characteristics, such as size effect, unique surface, and high aspect ratio, i.e., not being spherical [2]. Anisotropic metallic nanomaterials, in particular, find wide-range applications, including sensors [3,4], solar cells [5], bioimaging [6], photothermal therapy [7], surface enhancement and Raman scattering [8], and more [9]. In catalytic applications, it's important to prepare anisotropic nanomaterials with well-defined size and shape in order to enhance catalytic efficiency and selectivity [10]. Anisotropic metallic nanomaterials have been successfully employed in various catalytic reactions, including hydrogenation [11], oxidation [12], cross-coupling [13], and electron transfer [14]. Catalytic esterification reactions play a significant role in diverse industrial applications. Simple esters can be obtained by reacting carboxylic acid with alcohol using homogeneous or heterogeneous catalytic systems [15]. Esters find utility as softeners, emulsifiers, surfactants, detergents, dispersants, and solvents [16]. Methyl acetate, in particular, is a highly demanded ester used in industries such as glue, dye, perfume, and solvent production. It is also employed in the synthesis of polyesters and cellulose acetate [17]. The esterification of acetic acid with methanol is a straightforward reaction for producing methyl acetate. Both homogeneous and heterogeneous catalysts have been employed for methyl acetate production. Mineral acids are widely used as a homogeneous catalyst for acetic acid esterification [15]. However, such catalysts have drawbacks, including corrosive properties and challenges in product recovery. Moreover, mineral acid-based catalysts can reduce the purity of the products [18]. Heterogeneous catalytic systems, like solid acid catalysts and ion exchange resins, are often used in esterification and organic transformations because they are very good at absorbing substances and making the transformation process more efficient [15]. Nevertheless, the surface distortion of heterogeneous catalysts can reduce efficiency and selectivity [20]. Metal catalysts have gained significant attention for esterification processes [21], and several metallic nanoscale heterogeneous catalysts have been established to achieve high efficiency and selectivity in esterification transformation [22-24]. Copper nanoparticles exhibit significant catalytic properties due to their unique metallic properties and quantum size. The design of monodisperse copper nanoparticles has garnered attention in both industry and academia [25]. The catalytic performance of copper nanoparticles has been reported in various reactions and transformations, including organic synthesis [26,27], antifungal [28], biomass conversion [29], reductions [30], dehydrogenations [31], CO oxidation [32], organic compound degradation, and carbon dioxide reduction [33]. While the synthesis of copper nanotubes has been explored for catalytic applications with moderate to excellent results [34 -38], few studies have investigated the catalytic esterification transformation using isotropic bulk catalysts [39,40] and nanoscale [41], copper-based catalysts. To the best of our knowledge, there is no reported study on the catalytic esterification of acetic acid with alcohol utilizing copper nanocubes as a heterogeneous catalytic system. Therefore, our current study aims to design silica-supported copper nanotubes under green conditions and using environmentally friendly reagents. The copper nanocubes will be employed as a heterogeneous catalyst for the esterification of acetic acid with methanol to produce methyl acetate.

2. Experimental part

2.1. Chemicals

Di-n-butyl sulfide (C₈H₁₈S) (99%), copper chloride (CuCl₂), methanol (CH₃OH) (reagent grade, 99%), glacial acetic acid (CH₃COOH), *L*-ascorbic acid (C₆H₈O₆), and silica SiO₂ (MCM-41, pore size 0.98 cm³/g) were all purchased from the Sigma-Aldrich company. All chemicals were used without requiring further purification.

2.2. Catalyst synthesis

The synthesis of copper nanocubes in an aqueous solution involved the use of copper II chloride, *di-n*-butyl sulfide, and *L*-ascorbic acid as metal precursors, stabilizers, and reducing agents, respectively. The ratio between copper(II)chloride, *di-n*-butyl sulfide, and *L*-ascorbic acid was 1:10:10 by moles. Approximately 0.42 g of CuCl₂ was added to 30 mL of deionized water and degassed using N₂ gas for 15 minutes. Then, 4.54 g of *di-n*-butyl sulfide was added to the blue solution of CuCl₂ and stirred for 5 minutes using a magnetic stirrer. Approximately 5.59 g of ascorbic acid was dissolved in 10 mL of deionized water and added dropwise with continuous stirring to the solution of the metal precursor and stabilizer. The color gradually changed from blue to colorless and then to a faint brown upon the addition of ascorbic acid due to the reduction of copper. The addition was continued under N₂ gas and stirred for 5 minutes. Subsequently, the solution was covered by aluminum foil and left undistributed for 24 hours.

2.3. Catalyst support for silica

Silica (0.5 g) was dried in a vacuum oven under N₂ gas at 400 °C for 12 hours. The dried silica was allowed to cool to room temperature. Afterwards, the copper nanocube solution was added to the silica and stirred under N₂ gas for 12 hours. The solution above the silica turned from light brown to colorless, indicating the successful loading of copper-NCs on the silica. The mixture was then filtrated, and the collected product appeared as a brown powder.

2.4. Catalytic reactions

In a typical experiment, catalyst Cu-NCs on SiO₂ (0.1 g) was added to a solution of target organic compounds (acetic acid) (5 mL) and methanol (as solvent and reactant) (30 mL) in a 100 mL Schlenk flask. The flask was connected to a two-way stopcock, which was in turn attached to a rubber balloon containing N₂. The flask was evacuated for a few minutes while being stirred, and the reaction was carried out for 24 hours at room temperature. The reaction was conducted by stirring under N₂ gas. Samples were collected at 0, 10, 20, 30, 60, 120, 720, and 1440 minutes and subsequently analyzed by chromatography-mass spectrometry after filtration. Control reactions were also performed without a catalyst and with bare Cu-NCs (without silica as a support system).

2.5. Instrumentations

Gas chromatography and mass spectrometry data were recorded using a Shimadzu gas chromatography and mass spectrometry detector. The column used was a high-temperature DV-5. To investigate the size distribution of the synthesized metallic and bimetallic nanoparticles, a JEOL JEM-1230 transmission electron microscope operating at 80 kV of acceleration voltage with a maximum magnification of 600 KX was used. The crystal structures were analyzed by XRD (Bruker Smart Apex II-D8 with an Oxford 700 cold stage).

3. Results and discussion

Designing anisotropic metallic nanomaterials under green conditions presents a significant challenge. Therefore, rational optimization experiments were carried out in this study. The optimization process involved the selection of metal precursors, types and concentrations of

reducing agents, and the study of stabilizer ligands, particularly thioester compounds, which exhibited excellent performance in terms of copper nanocubes (Cu-NCs) size (15×5 nm) and shape distribution, as shown in Figure 2. Additionally, various green reducing agents such as poly(methylhydrosiloxane), sodium hypophosphite, and natural products such as green tea, coffee, cinnamon, and curcumin extracts were optimized, and L-ascorbic acid was chosen for its efficiency in the Cu-NCs synthesis. The color of the copper precursor changed from blue to light brown upon the addition of the reducing agent. The importance of additive reducing agents provides evidence to get good results for synthesized copper nanocubes in terms of size and shape and the reduction of the metal precursor; this can be assessed due to the appearance of the reduction peak, which indicates the formation of metallic copper nanocubes, and it is just a normal reduction equation from Cu^{+2} to Cu^0 . as illustrated in Figure 1a.

a)



b)

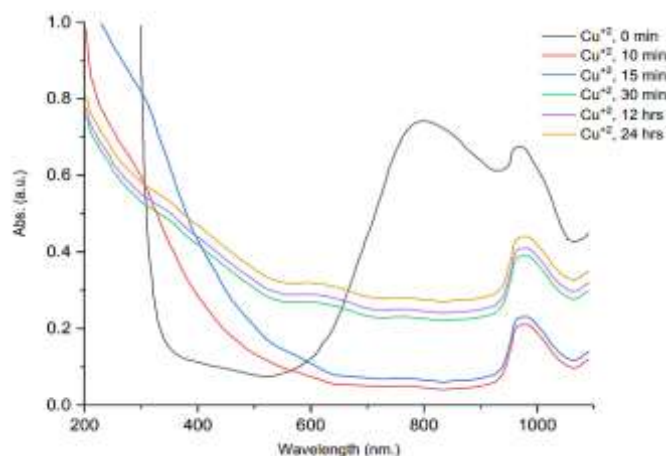


Figure 1 : (a) Colour change due to the reduction of the metal precursor and the Cu-NCs production from Copper II chloride solution to Cu-NCs faint brown colour. (b) UV-Vis spectrum of copper metal precursor and after addition of reducing agent

The conversion of copper chloride to copper nanocubes was observed by UV-Visible and TEM. The optimized mole ratio was found to be 1:10 (CuCl_2 : ascorbic acid), which resulted in the immediate reduction of the copper. The UV-Visible spectrum in Figure 1b shows the reduction of the copper precursor after 10 minutes of adding ascorbic acid. The peak at 780 nm disappeared, indicating the reduction of copper and the presence of Cu^{+2} , while another peak between 550 and 600 nm emerged in the literature. The peak of UV-Visible for copper nanomaterials was determined between 550 and 600 nm due to the plasmonic resonance of the nanoscale of the copper [44], and it is indicating the formation of carbon copper nanocubes in

the current study. Additionally, an important observation from the spectrum is the increase in Cu-NCs concentration and UV-Visible absorbance over time, as shown in Figure 1 b.

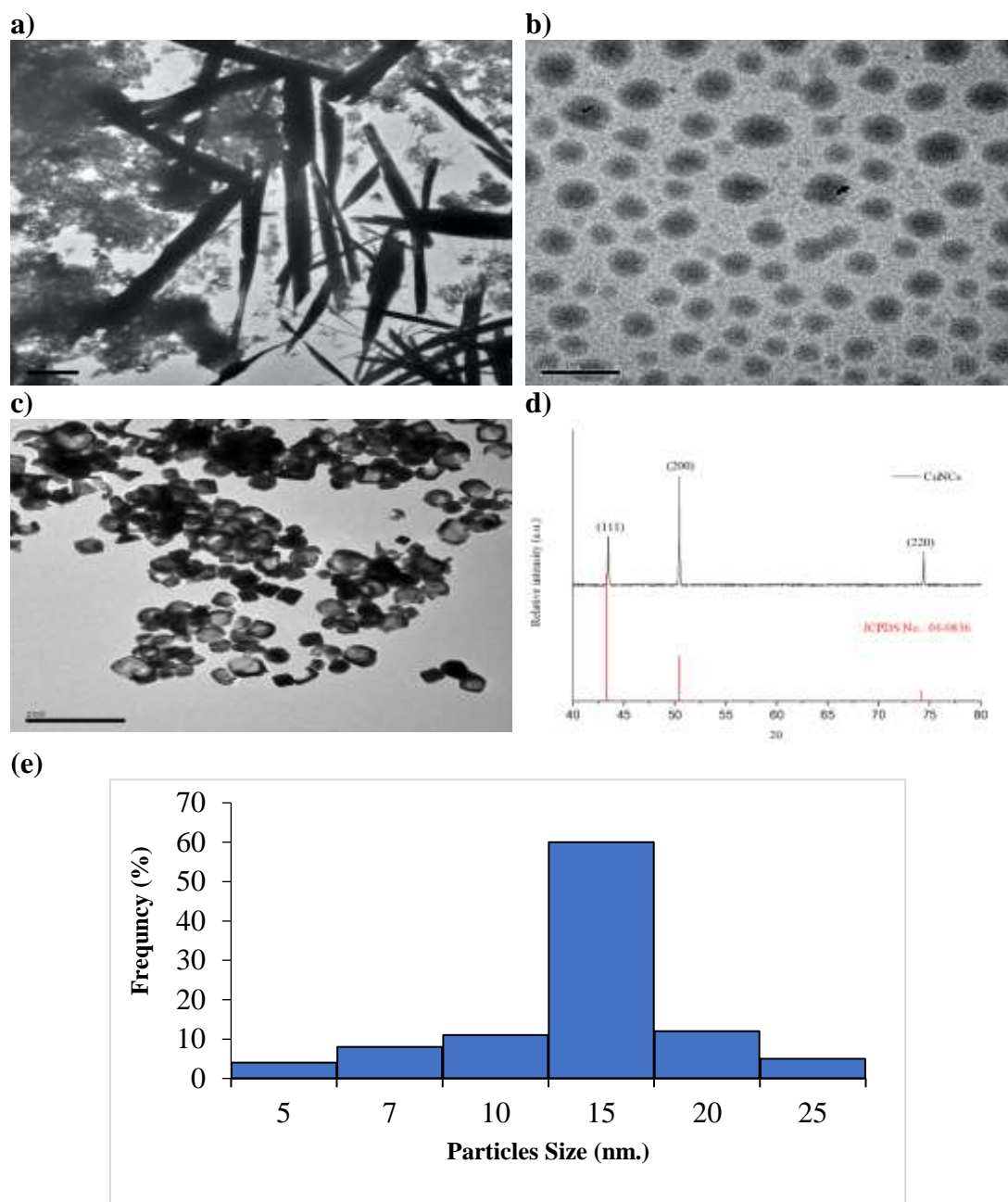


Figure 2: (a) TEM image of CuCl₂. (b) TEM image of copper chloride after 10 minutes of ascorbic acid addition. (c) TEM image of Cu-NCs after a 24-hour reaction. (d) XRD spectrum for the final Cu-NCs after 24 hours' addition of ascorbic acid. (e) Histogram of particle size of Cu-NCs.

The conversion of copper from the metal precursor to the final Cu-NCs was monitored using TEM, as shown in Figure 2 (a, b, and c). The TEM images proved the reduction of copper chloride (Figure 2a) to copper nanocubes (2b) and the resulting Cu-NCs obtained after 24 hours at room temperature (2c). It is worth noting that some of the CuNPs exhibited fusion, as can be seen in Figure 2c, due to the intensity of the electron beam. The XRD pattern revealed three prominent peaks corresponding to 111, 200, and 220, which indicated the face-centered cubic (FCC) shape (JCPDS No.: 04-0836) [45-48]. Although some of the CuNCs displayed irregular

shapes due to the use of green reagents during synthesis, the efficiency of the resulting copper NCs is determined by their catalytic application. This study successfully synthesized CuNCs in an aqueous solution using *L*-ascorbic acid as a green reducing agent. The stability of CuNCs was maintained for 3 months without any precipitation or color change. Silica was employed as a support material for the nanocubes following several optimization reactions to achieve the highest metal load, stability, and reactivity due to the additional surface area that silica provides to enhance the stability of the Cu catalyst and its recyclability. The nanoscale catalyst becomes a heterogeneous catalyst, which has the advantage of recycling and reusing with a simple wash with methanol. In addition, the recycled catalyst showed reactivity for three catalytic cycles without a decline in performance. The catalyst was used for the esterification reaction, an essential step in the biodiesel production process. The catalytic reaction was carried out, and samples were analyzed at different reaction times, as presented in Table 1. The conversion of acetic acid to methyl acetate occurred over Cu-NCs / SiO₂ at room temperature, as illustrated in the below equation (1).

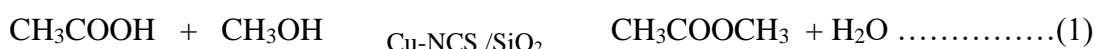


Table 1 : The conversion percentage of acetic acid with different times and catalysts

Conversion n%	Catalyst	Reaction time (minutes)						
		0	10	20	30	60	720	1440
	No catalyst	0	0	0	0	<1	<1	<1
	Only SiO ₂	0	0	0	0	<1	3	4
	Cu-NCs/SiO ₂	0	15	21	32	55	71	80

Different catalytic reactions were carried out to optimize the reaction time and ensure that the designed catalyst was responsible for the conversion [44-47]. The result showed that the highest conversion percentage of acetic acid and methanol to methyl acetate was obtained with Cu-NCs at SiO₂ after 1440 minutes' reaction time under nitrogen at room temperature. Furthermore, no conversion was observed without catalyst or with silica alone, which indicates the responsibility of Cu-NC at SiO₂ for the conversion process. The conversion percentage was characterized by GCMS, as shown in Figure 3. The data were obtained by using the concentration of methyl acetate (the desired product) measured by calculating the area under the peak in the GC-MS. The GCMS results showed the remaining 20% of acetic acid, which means that the conversion is 80% to methyl acetate over Cu-NCs at the SiO₂ catalyst. Other studies of the esterification process to produce methyl acetate showed the same efficiency or a slightly higher yield [15-18]. However, the catalysts used were either corrosive (mineral acid), which cannot be reused, or required high temperatures to achieve a high conversion percentage. Therefore, the heterogeneous copper nanocube-based catalyst (recoverable catalyst) used in this study has shown high catalytic efficiency in environmentally friendly conditions.

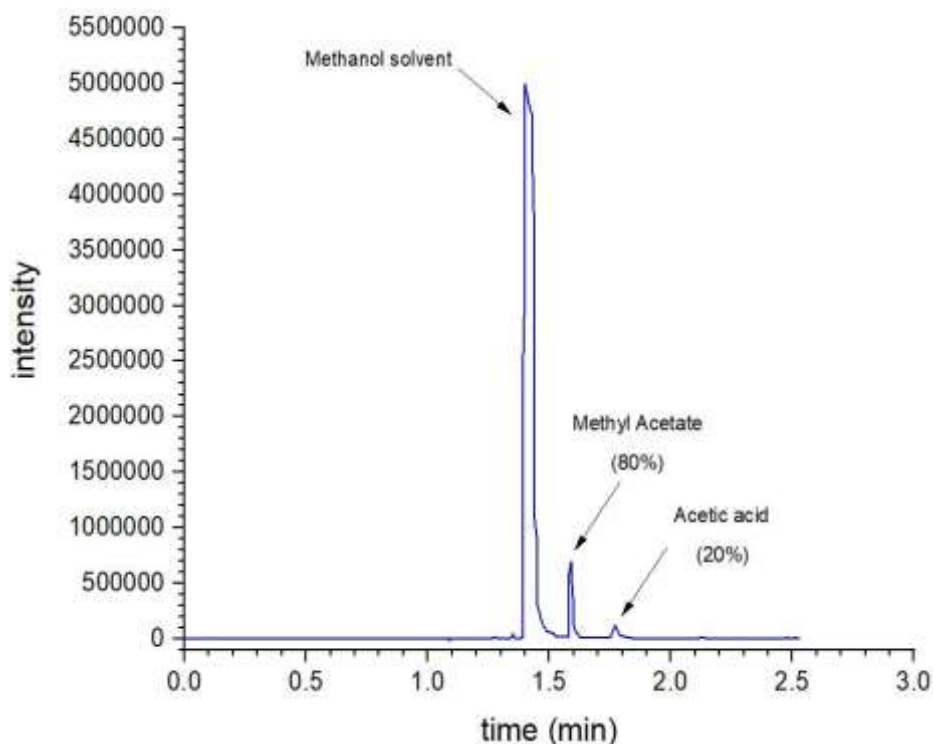


Figure 3: The GCMS chart of the esterification process after 24 hours of reaction time at room temperature

4. Conclusion

This study successfully achieved two significant goals. Firstly, it synthesized nanoscale CuNCs using moderate reagents and reaction conditions, employing ascorbic acid as a reducing agent and water as a solvent. Secondly, the catalyst was synthesized at room temperature, further enhancing its environmentally friendly properties. The synthesized silica-supported catalyst was utilized for the esterification of acetic acid at room temperature. The catalytic reaction involved the use of acetic acid and methanol as a reactant and solvent, respectively. A remarkable high conversion percentage was achieved at room temperature, which indicates the efficiency of the catalyst. The nanoscale size of the copper catalyst, coupled with its cubic shape, played a crucial role in attaining high catalytic efficiency.

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Authors' declaration

Conflicts of interest: None - We hereby confirm that all the Figures and Tables in the manuscript are our own work.

Author contributions statement

This work has been done in collaboration among the three authors. H.A.A. diagnosed the case for study, collected the samples, did the investigation, and wrote the original draft. A.Z.M.A. reviewed and edited the manuscript and supported it with resources for drafting, S.S.M.A. data analysis, and reviewing the manuscript.

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