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Research Article

Lignocellulosic Micro- and Nanomaterials as Copper Frames for the Evaluation of the Copper(I)-Catalyzed Azide-Alkyne Cycloaddition

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Copper was immobilized onto carboxymethyl cellulose, nanofibrillated cellulose, TEMPO-nanofibrillated cellulose, and lignin. The lignocellulosic frames were used with the aim of providing an effective support for catalyst copper and allowing its further reutilization. Each organic support was successful and effective in the coupling of copper with the exception of lignin. These complexes were used as heterogeneous catalysts to produce 1-benzyl-4-phenyl-1H-[1,2,3]-triazole from the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) between benzyl azide and phenylacetylene. Each reaction was carried out in water and acetonitrile. Those performed in water were completed in 15 minutes while those done in acetonitrile were allowed to react overnight, reaching completion in less than 20 hours. The yields for Cu-CMC resulted in over 90% for those reactions performed in acetonitrile. All catalysts were easy to recover except Cu-lignin which could not be filtered or extracted from the reaction effluent.

1. Introduction

The "Huisgen click" reaction refers to an azide-alkyne 1,3-dipolar cycloaddition. This reaction has many useful applications for drug discovery [1], polymer synthesis [2], and material science [3], among other biological applications [4, 5]. However, this reaction often requires high temperatures, has a low reaction rate, and typically produces a mixture of 1,5-substituted and 1,4-substituted triazoles [6].

Copper (Cu) based catalyst for the "Huisgen click" reaction has received significant attention during the last decade due to its versatile reactivity and much lower cost compared with noble metals, such as Pd and Rh. The rate of this copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) is increased by a factor of 10^7 relative to the purely thermal process [6]. Most CuAAC procedures involve in situ reducing agents to reduce Cu(II) salts in the generation of Cu(I) catalysts [7]. This reaction is quite insensitive to its environment and is also unaffected by most functional groups, so it may be performed in an aqueous or organic solution. However,

it is most commonly performed in a water/alcohol mixture [6, 8, 9], though, without somehow immobilizing the copper on a homogeneous support, this CuAAC reaction is still very limited due to the low recoverability of copper from the product [10].

In general catalytic metal particles have been immobilized on solid supports that include the following: silica, alumina, zirconia, ceria, zeolites, glass fibers, and synthetic polymers [11–14]. The concept of sustainable chemistry is opening incredible opportunities for supporting materials coming from renewable natural polymers. Cellulose-based materials were studied as a support material for metal catalysts some years ago [15]. In recent years, the utilization of cellulose nanomaterials, such as cellulose nanofibers and cellulose nanocrystals, has demonstrated excellent performance to be used as scaffold for metal nanoparticles in catalysis [16–18]. Shen et al. in 2010 used $CuSO_4$ reduced by sodium ascorbate to catalyze *O*-acetyl-*α*-L-arabinopyranosyl azide and phenyl acetylene and found yields unsatisfactory at 54% [19]. The group then immobilized Cu onto microcrystalline

cellulose as a catalyst, and the reaction (performed in water at 60°C) produced a 93% yield, showing that a cellulose-supported copper catalyst is favorable. The group also reused the catalyst and, after five cycles, the yield was still favorable at 84%, displaying excellent recoverability of the Cu(0)-cellulose catalyst [20].

Reddy et al. used the same procedure and materials as Yu et al. to create the Cu(0)-cellulose catalyst and had similar results in their catalyst formations, with Cu 2P X-ray photoelectron spectroscopy (XPS) spectra peaks around 932.7 eV. However, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis in both studies show that Yu et al.'s Cu(0)-cellulose had almost double the amount of copper compared to Reddy et al.'s at 0.730 mmol/g and 0.368 mmol/g, respectively [20, 21]. This could be due to the type of wood the cellulose was drawn from and, correspondingly, the amount of carboxylate groups on the cellulose fibers.

Koga et al. created a cellulose-supported Cu(I) catalyst using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nanofibrillated cellulose (TNFC). The azide-alkyne pair of benzyl azide and phenyl acetylene reacted in an aqueous solution of sodium ascorbate containing the Cu(I)-TNFC catalyst; the copper content of the catalyst used in the reaction was 10 μmol. Through NMR analysis, the product was found to be entirely 1-benzyl-4-phenyl-1H-[1,2,3]-triazole, the desired product [17]. This indicates both the procedure and catalyst were very effective for this azide-alkyne cycloaddition.

Zhong et al. in 2013 used carboxymethyl cellulose (CMC) to immobilize copper that displayed excellent antimicrobial properties against *Escherichia coli*. Then, in 2015, Zhong et al. developed an efficient drying process for Cu-TNFC and Cu-CMC complexes—which was developed using the same procedure from Zhong et al. in 2013. The results of this procedure, through XPS analysis, showed that the oxidative state of copper in the final product was Cu$^+$, which was the oxidative state of copper in the research previously discussed by Koga et al. in 2012. In this study, copper nanoparticles were supported on lignin and three different kinds of cellulose (CMC, NFC, and TNFC) for the cycloaddition of benzyl azide and phenyl acetylene. Similar processes to the production of Cu-CMC [22], drying of the Cu-TNFC and Cu-CMC [23], and catalyst performance test of CuAAC [17] were used in this research.

2. Materials and Methods

2.1. Materials.
Sodium carboxymethyl cellulose (Na-CMC) with average molecular weight of 90,000 g/mol was purchased from Sigma-Aldrich, USA; nanofibrillated cellulose (NFC), 2.8 wt%, from the University of Maine, USA; TEMPO-nanofibrillated cellulose (TNFC) gel, 0.96 wt%, from Forest Products Laboratory, USA; lignin, alkali from Sigma-Aldrich, USA; copper sulfate pentahydrate (CuSO$_4$·5H$_2$O) from Fisher Scientific, USA; sodium borohydride (NaBH$_4$), 0.5 M, from Acros, USA; ethanol (reagent alcohol, 95%) from Sigma-Aldrich, USA; tert-butanol (99.5%) from Acros, USA; benzyl azide (94%) from Alfa Aesar, England; phenyl acetylene (98%) from Alfa Aesar, England; sodium cyanoborohydride (NaBH$_3$CN) from Sigma-Aldrich, USA.

2.2. Preparation of Copper Catalysts

2.2.1. Preparation of Copper-Carboxymethyl Cellulose.
Sodium carboxymethyl cellulose (Na-CMC) (1 g) was suspended in deionized water (49 mL). After that, CuSO$_4$ (aqueous, 15 mL, 0.1 M) was added dropwise to the solution under constant stirring. Once all the CuSO$_4$ had been added, mixing immediately ceased, and the solution rested for 14 h. Sodium borohydride (aqueous, 10 mL, 0.5 M) was added slowly under constant stirring over 30 min in order to reduce the oxidation state of copper [22].

2.2.2. Preparation of Copper-Nanofibrillated Cellulose.
Nanofibrillated cellulose (NFC) gel (1 g, 2.8 wt%) was suspended in deionized water (10 mL). After that, CuSO$_4$ (aqueous, 4 mL, 0.1 M) was then added dropwise to the solution under constant stirring for 1 h. Sodium borohydride (aqueous, 3 mL, 0.5 M) was added as a reducer. Once added, the suspension underwent constant stirring for 30 min.

2.2.3. Preparation of Copper-TEMPO-Nanofibrillated Cellulose.
TEMPO-nanofibrillated cellulose gel (5 mL, 0.96 wt%) was suspended in deionized water (10 mL). After that, CuSO$_4$ (aqueous, 4 mL, 0.1 M) was then added dropwise to the solution under constant stirring for 1 h. Next, to reduce the oxidation state of copper, sodium borohydride (aqueous, 3 mL, 0.5 M) was added and stirred for another 30 min.

2.2.4. Preparation of Copper-Lignin.
Lignin (1 g) was suspended in deionized water (10 mL). After that, CuSO$_4$ (aqueous, 4 mL, 0.1 M) was then added dropwise to the solution under constant stirring for 1 h. Lastly, sodium borohydride (aqueous, 3 mL, 0.5 M) was added slowly and then stirred with the suspension for 30 min to ensure all the copper had been reduced.

2.3. Drying and Purifying the Copper Catalysts.
Each suspension was then centrifuged and the upper liquid layer was removed. The solids that remained were then redispersed in water (50 mL) and centrifuged again at 8000 rpm for 5 min. The upper clear solution was removed, and ethanol (25 mL) was mixed with the solid in the bottom of the vial. The vial was centrifuged again at 8000 rpm for 5 min, and the upper clear solution was subsequently removed. Ethanol was again mixed, and, after waiting for two hours upon mixing, the solution was centrifuged at 8000 rpm for 5 min. The upper liquid was then removed. This process was repeated using tert-butanol. The solid that remained from each suspension was then stored in a vacuum for 2 days to prevent oxidation and to allow the tert-butanol to dry. After the solids were dried under vacuum, they were placed in a freeze-dryer for 3 days [23]. Note that this process was only used to dry Cu-CMC, Cu-NFC, and Cu-TNFC. The Cu-lignin suspensions were not able to be separated from the solvent after centrifugation; therefore, the lignin suspension was placed directly in the freeze-dryer.

2.4. Catalyst Performance Test.
Sodium cyanoborohydride (aqueous, 3.3 mM, 30 mL) was used to pretreat Cu-CMC
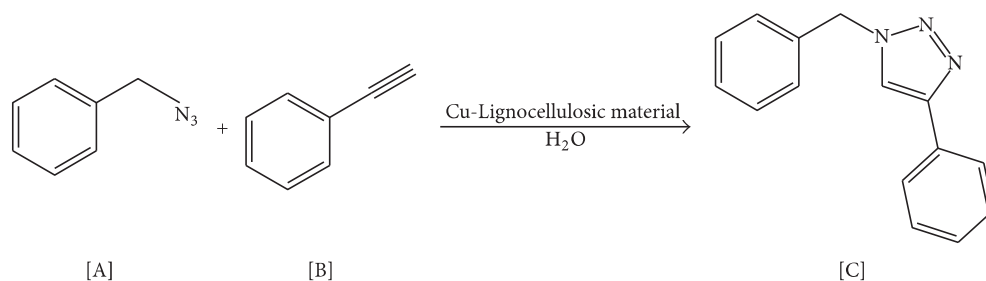
FIGURE 1: Illustration of the CuAAC of benzyl azide and phenylacetylene to produce 1,4-BPT, where [A]: benzyl azide, [B]: phenylacetylene, and [C]: 1-benzyl-4-phenyl-1H-[1,2,3]-triazole (1,4-BPT).

(6 mg), Cu-NFC (11 mg), Cu-TNFC (14 mg), and Cu-lignin (200 mg)—all separately—at 70°C for 20 min prior to performing the CuAAC reaction. For the CuAAC reaction, benzyl azide (125 μL, 1.00 mmol) and phenylacetylene (110 μL, 1.00 mmol) were added to each solution under constant stirring at 70°C [17]. The CuAAC reaction is represented in Figure 1. The progress of the reaction was monitored by thin layer chromatography (TLC, hexane/EtOAc, 19 : 1). After the complete disappearance of benzyl azide, the catalyst was recovered from the mixture by filtration and washed with water (2 × 10 mL) and acetone (2 × 10 mL) and then allowed to dry in a vacuum. The filtrate was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried (MgSO$_4$) and filtered and filtrate was concentrated in vacuum [20]. The crude product was purified by filtration through a short plug of silica gel eluting with EtOAc to yield 1-benzyl-4-phenyl-1H-[1,2,3]-triazole (1,4-BPT).

This process was then repeated using Cu-CMC and scaled up by a factor of 5 in order to reduce human error. In addition to scale-up, the recovered catalyst was reused twice for the same reaction to analyze catalytic decay.

This scaled-up process was also repeated using Cu-CMC in 30 mL of acetonitrile, a common solvent medium for CuAAC, instead of 30 mL of water. This was done to compare with other literature, as water is not typically used as the solvent in this CuAAC since copper easily dissolves in water. However, water is a very desirable reaction medium due to its abundance and environmental sustainability.

2.5. Characterization. The copper loading on each catalyst support was determined using Varian Vista-PRO CCD simultaneous inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Palo Alto, USA). In order to prepare these samples for ICP-OES, 30 mg of each catalyst was dissolved in 1 mL of nitric acid (71 wt%). When the solid complexes were completely dissolved, the solution was diluted with 99 mL of deionized water and 15 mL of this solution was then used for ICP-OES analysis.

The oxidation state of copper on each catalyst was determined using Physical Electronics VersaProbe 5000 X-ray Photoelectron Spectroscopy (XPS) system with a monochromatic Aluminum Kα X-ray source (Chanhassen, MI, USA). The base pressure in the high vacuum analysis chamber was around 2 × 10^{-6} Pa. An Aluminum X-ray source of 1486.6 eV

was used for photoelectron excitation with X-ray power of 25 W. Pass energies of 117.4 eV for survey scan and 23.5 eV for detailed scan were used for the data acquisition with energy steps of 0.5 eV for survey scan and 0.05 eV for detailed scan, respectively. PHI MultiPak software was used for element identification and peak fitting. The C1s peak at a binding energy of 284.8 eV was used as the internal reference. A Shirley-type background was subtracted from the spectra and Gauss-Lorentz curves were used to fit the spectra.

The solid product from the CuAAC reaction was dissolved in deuterochloroform and nuclear magnetic resonance (^{1}H NMR) measurements were taken using a 400 MHz Agilent Technologies NMR, Model Number 400/54/ASP. Data analysis was performed using Agilent Technologies Software VNMRJ, Version 2.4, Revision A.

2.6. Yield Determination. The yield of each reaction was determined in the following equation:

$$\frac{\text{Theoretical Yield} - \text{Actual Yield}}{\text{Theoretical Yield}} \times 100. \qquad (1)$$

3. Results and Discussion

3.1. Production of Copper Catalysts. ICP-OES analysis calculated the amount of copper on each catalyst. Three samples of each complex were used in order to gain an accurate knowledge of the loading of copper onto each organic support. Figure 2 displays the results from ICP-OES. The number above each bar indicates the average mmol of Cu per gram of catalyst. The error bars indicate the standard deviation for all the trials for each sample. These error bars represent the amount of variation of copper throughout the catalyst. The results are excellent when compared to literature.

Yu et al. used microcrystalline cellulose as the platform to attach copper, and the copper loading onto the microcrystalline cellulose only resulted in 0.730 mmol Cu/g catalyst [20]. All of our compounds except Cu-lignin (due to the procedure in which it was created) have higher copper loadings than this, and CMC has over 2.5 times the copper loading of the microcrystalline cellulose. From these results, it can be concluded that CMC is the best organic compound on which to immobilize copper nanoparticles. This is likely due to the presence of high number of Na-carboxyl groups
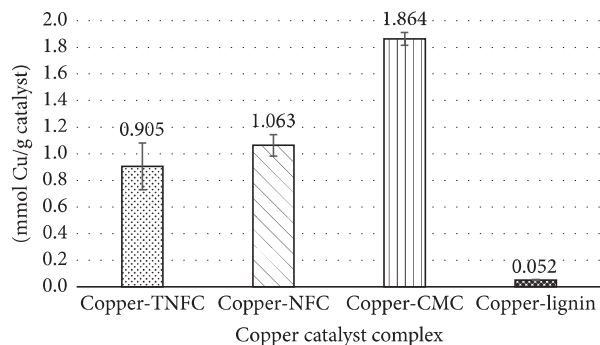
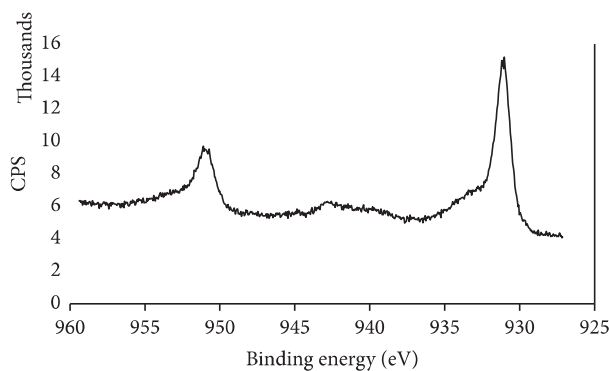Figure 2: Amount of copper per gram of catalyst on each hybrid material.

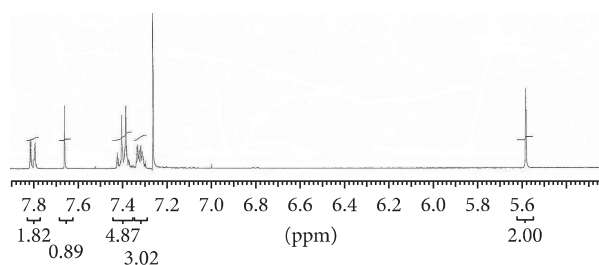Figure 3: XPS spectra of Cu-CMC.

Figure 4: NMR results for material produced from procedure used in this research.

Table 1: Yield information of each CuAAC using different catalysts.

Catalyst proposed	1,4-BPT yield (mg)	Yield percentage
Cu-CMC	131	56%
Cu-NFC	85	36%
Cu-TNFC	136	58%
Cu-lignin	90	39%

Table 2: Results of CuAAC using and reusing Cu-CMC.

Catalyst use	Reaction time	Yield percentage
1	10 min	45%
2	20 min	43%
3	150 min	38%

that can facilitate the copper reduction and therefore its further availability.

As determined from XPS the state of oxidation was Cu(I) for all complexes. There were strong peaks around 931-932 and 950-951 with a weak satellite peak between the two around 943. This weak satellite peak was the determining factor for the oxidation state because it is unique to the Cu(I) oxidation state only. Figure 3 displays the XPS data graphically for Cu-CMC. All data for the remaining complexes are very similar and therefor will not be displayed along with the Cu-CMC.

3.2. Catalyst Performance Test

3.2.1. Using Water as Media for the Reaction. The reaction time was outstanding for each catalyst, with each reaction reaching completion in 15 minutes. Compared to Koga et al., who used softwood-derived TNFC as a catalyst support for the same reaction, our copper-cellulose complexes catalyzed the reaction 5 min faster [17]. However, the yields for 1,4-BPT were not satisfactory. Table 1 presents information regarding the yields pertaining to each catalyst.

One thing to note as well is that the Cu-lignin was irrecoverable from the reaction. It appears to have dissolved in the aqueous layer.

Table 2 shows the results of the scaled-up reaction using Cu-CMC and the same reaction reusing the catalyst.

These results show that the first reuse of the catalyst is still very effective as the reaction time was still very fast, only increasing by 10 minutes. However, after reusing the catalyst once again, the reaction time increased greatly to 150 min suggesting the catalyst is not be reused more than once.

The low yields could be due to the extraction and purification process of the product, as there is much room for human error in this procedure. When using an internal standard of 1,4-dimethoxy benzene, NMR analysis showed yields of over 80% 1,4-BPT. This indicates that improvements can be made to purification in order to isolate the entire desired product that is formed.

The results of the ^{1}H NMR analysis from Cu-CMC as catalyst were as follows: δ_H ppm: 7.80 (d, 2H), 7.66 (s, 1H), 7.36–7.42 (m, 5H), 7.34–7.29 (m, 3H), and 5.58 (s, 2H). The data are shown graphically in Figure 4; the numbers below the x-axis are the areas under each spike (or group of spikes) and represent the number of hydrogen atoms on each carbon. The most indicative datum on Figure 4 is the spike around 5.6 ppm. This is the carbon with two single bonds connecting the phenyl group to the azide group. Since it is known that there are two hydrogen atoms at this point and therefore the area under the spike will be exactly 2, this data was implemented into the analysis and all other areas under each spike were determined using this data as the standard. The large spike around 7.25 ppm is from the solvent, deuterochloroform, used to dissolve the product for analysis. Since every single area under each spike or group of spikes concurred with literature [17, 24], the results indicate the product was entirely 1,4-BPT using each copper complex as the catalyst.

TABLE 3: Yield information using acetonitrile as reaction medium.

Catalyst proposed	1,4-BPT yield (mg)	Yield percentage
Cu-CMC	1070	91%
Cu-TNFC	872	74%

The reaction completely favors the formation of 1,4-substituted triazoles as well, differing from the thermal reaction which often results in a mixture of 1,4-substitued and 1,5-substituted triazoles [6].

3.2.2. Acetonitrile as Media for the Reaction. Considering that the highest yields in water as media were for Cu-CMC and Cu-TNFC, they were tested in acetonitrile to evaluate differences. The results in this regard are presented in Table 3. When using acetonitrile as the solvent for the reaction and CMC-Cu as catalyst, 5 mmol of reactant yielded 1.07 g (91% yield) of 1,4-BPT. These results are very comparable to other researches [24, 25] concluding that CMC is an effective support for copper to be used as a catalyst. In terms of Cu-TNFC, yields were less satisfactory at 74%, though much improved from the reaction in a water medium.

4. Conclusions

Cu-cellulose was easily prepared using CMC, NFC, TNFC, and lignin. These complexes were then used as catalysts in the CuAAC between benzyl azide and phenylacetylene to produce 1,4-BPT. Water and acetonitrile as media for the reaction were used. In water media, the catalysts, with the exception of lignin, were easy to recover, displaying the low hazardous impact the reaction has on the environment. The reaction was complete in 15 minutes for each copper complex, showing the excellent catalytic ability of each heterogeneous catalyst. Cu-CMC and Cu-TNFC displayed the highest yields and were subsequently used as catalysts when acetonitrile was utilized as media for the reaction. The reaction in this case needed longer time to be completed and the yield resulted higher for Cu-CMC. Based on the process used to fabricate the hybrid Cu-cellulose materials, CMC appears to be the best support for copper of the four organic compounds used as it held the most copper due to its higher number of Na-carboxyl groups and yielded one of the highest amounts of 1,4-BPT. Further investigation will be directed on the improvement of copper attachment on the lignocellulosic raw material for the specific application in the catalysis field.

Abbreviations

1,4-BPT: 1-Benzyl-4-phenyl-1H-1,2,3-triazole
CMC: Carboxymethyl cellulose
CuAAC: Copper azide-alkyne cycloaddition
TEMPO: 2,2,6,6-Tetramethylpiperidine-1-oxyl radical
NFC: Nanofibrillated cellulose
TNFC: TEMPO-nanofibrillated cellulose
ICP-AES: Inductively coupled plasma atomic emission spectroscopy
ICP-OES: Inductively coupled plasma-optical emission spectrometry
NMR: Nuclear magnetic resonance
TLC: Thin layer chromatography
XPS: X-ray photoelectron spectroscopy.

Conflicts of Interest

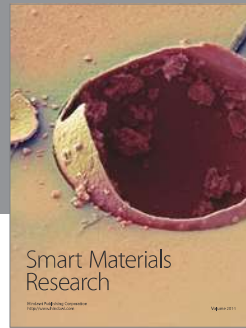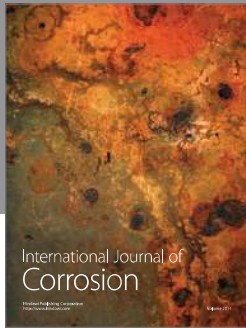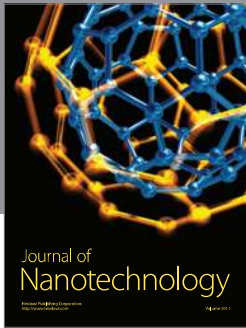The authors declare that they have no conflicts of interest.

Acknowledgments

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