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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Poly(hydroxamic acid) Functionalized Copper Catalyzed C-N Bond Formation Reactions

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Highly active poly(hydroxamic acid) functionalized copper catalysts were synthesized by the surface modification of khaya cellulose through graft copolymerization and subsequent hydroximation processes. The prepared catalysts were well characterized by FTIR, FESEM, HRTEM, ICP-AES, UV-vis and XPS analyses. The supported catalysts effectively promoted C-N bond formation reactions and provided excellent yields of the corresponding products under mild reaction conditions. The catalysts were easy to recover from the reaction mixture and were reused several times without any significant loss of their catalytic activity.

Introduction

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The addition reaction so-called Click [1] and Aza-Michael [2] reactions are important C-N bond formation reactions have a wide range application in the modern scientific communities [3]. Traditionally, different copper complex sources have been used for these reactions such as for Click reaction; Cu(II)/Cu(0) comproportionation [4], mixed Cu/Cu-oxide nanoparticles [5], in-situ reduction of Cu(II) to Cu(I) salts [6], for Michael reaction; AlCl₃ [7], PtCl₄·5H₂O [8], InCl₃/TMSCl [9], Bi(NO)₃ [10], boric acid [11], bases [12]. However, these homogeneous metal catalyzed reactions have several limitations like side products, a high cost of metal complexes, harsh conditions, long reaction times, metal leaching out into the reaction mixture, difficult to recover the catalyst and require large excesses of reagents or catalysts. Therefore, the use of heterogeneous catalysts for organic synthesis is rapidly growing over homogeneous catalytic systems because of their several advantages such as high stability and tolerant to harsh reaction conditions, reusability of the catalyst, environmental friendliness and easy to purify of the products [13]. Thus, heterogeneous metal catalysts have been utilized for the Click and Michael addition reactions. For instance, Zeolites [14], polymers [15], non-magnetic and magnetic supported Cu(I) [16], silica [17], TiO₂-nanotube [18], cellulose supported Cu(0) [19] have been used effectively for Click reaction; whereas for

Michael addition MOF-99 [20], silica sulfuric acid [21], Amberlyst-15 [22], cellulose-Cu(0) [23], polystyrene-AlCl₃ [24], doped natural zeolite [25], MCM-41 immobilized heteropoly acids [26], amine-functionalized silica supported Co(acac)₂ [27] proved good catalytic activity. Nevertheless, from green technology aspects, there is still a high demand to explore more efficient catalyst for chemical transformation reactions. Nowadays, scientists are continuing their effort to investigate low-cost environmental friendly and sustainable processes using renewable resources. In this perspective, natural biopolymers (cellulose) could be considered most acceptable material because it has some promising merits like large abundance in nature, low density, bio-renewability, universal availability, low-cost and interesting mechanical properties compared to the glass fibers [28]. Therefore, natural cellulose would be the perfect candidate to consider as a solid support for catalysts [29]. In addition, cellulose backbone can be chemically modified and suitable metals coordinating groups can be effectively introduced [30]. Currently, biopolymers like cellulose [31], starch [32] alginate [33], gelatin [34], and chitosan [35] derivatives have been used as supports for catalytic applications with acceptable catalytic performance along with some drawbacks. Eventually, it is particularly envisaged to unfold a more general, simple and convenient catalytic process which could be applicable to various substrates of different nature under pleasant and environment-friendly reaction conditions. Keeping this view, in this report we used copper anchored onto poly(hydroxamic acid) functionalized khaya cellulose as efficient heterogeneous catalysts for C-N bond formation via Click reaction [Cu(I)] of organic azide and terminal alkyne, and chemoselective Aza-Michael addition [Cu(0)] of aliphatic amines with α , β unsaturated compounds. The cellulose supported copper catalysts were found highly active as well as chemoselective in the C-N bond formation reactions. The catalysts were easy to

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[†]Electronic Supplementary Information (ESI) available: [IR and UV spectra of the catalyst and all NMR data of the products are available]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C6RA08155J Journal Name

recover and reused without significant loss of its catalytic activity.

Experimental

General information

All manipulations were done under atmospheric conditions if otherwise noted. Reagents and solvents were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system as a Milli-Q grade. CuSO₄·5H₂O was purchased from Aldrich Chemical Industries, Ltd. ¹H NMR (500 MHz), ¹³C NMR (125 MHz) spectra were measured with a BRUKER-500 spectrometer, Central laboratory, University Malaysia Pahang. The ¹H NMR chemical shifts were reported relative to tetra methylsilane (TMS, 0.00 ppm). The $^{13}\mathrm{C}$ NMR chemical shifts were reported relative to CDCl₃ (77.0 ppm). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Shimadzu ICPS-8100 equipment by the central laboratory, University Malaysia Pahang. FTIR spectra were measured with a Perkin Elmer (670) spectrometer equipped with an ATR device (ZnSe crystal), FIST, University Malaysia Pahang. XPS spectra were measured with a Scanning X-ray Microprobe PHI Quantera II, MIMOS, Kuala Lumpur, Malaysia. FE-SEM was measured with JSM-7800F, Central laboratory, University Malaysia Pahang, TEM was measured with HT-7700. Hi-Tech Instruments SDN BHD, Puchong, Malaysia. TLC analysis was performed on Merck silica gel 60 F 254. Column chromatography was carried out on silica gel (Wakogel C-200).

Materials

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Khaya fiber was obtained from local market at Kuantan, Pahang, Malaysia and was cut into small pieces (~0.5 cm). The raw fiber (150 g) was boiled with 17% NaOH (800 mL) for 6 h and repeatedly washed with distilled water. The resulting fiber was boiled with glacial acetic acid (800 mL) for 1 h and washed with distilled water. The dark color khaya cellulose was then bleached with hydrogen peroxide (300 mL) and 7% NaOH (500 mL) respectively and washed with distilled water (500 mL) for several times to obtain white color cellulose and was dried at 50 °C before use. Methyl acrylate monomer purchased from Aldrich and it was passed through column filled with chromatographic grade activated alumina to remove inhibitors. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich), methanol (Merck), sulfuric acid (Lab Scan), metal salts and other analytical grade reagents were used without purification.

Graft copolymerization 1

The khaya cellulose (3 g) was dispersed into 300 mL distilled water. The copolymerization reaction was carried out in 500 mL three-neck round bottom flask fixed with stirrer and condenser in thermostat water bath. Diluted sulfuric acid (1.1 mL, 50%) was added into the reaction mixture and it was heated at 55 °C. After 5 min, 1.1 g of CAN (10 mL aqueous solution) was added and the reaction mixture was stirred under nitrogen atmosphere. After stirring for further 20 min, 10 mL of methyl acrylate monomer was added into the

cellulose suspension and stirring was continued for another 4 h under nitrogen atmosphere. The mixture was cooled at room temperature when colorless cellulose supported poly(methyl acrylate) was precipitated out and the obtained precipitates were collected by glass filtration. The precipitates were washed several times with aqueous methanol (methanol: water = 4:1) and dried at 50 °C to get a constant weight [36].

Synthesis of the poly(hydroxamic acid) ligand 2

The hydroxylamine solution was prepared by dissolving 12 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCI$) in 300 mL of aqueous methanol (methanol: water = 4:1). An aqueous solution of NaOH (50%) was added at cold condition into the hydroxylamine solution and the resulting NaCl precipitates were removed by filtration. The pH of the reaction was adjusted to pH 11 by control addition of NaOH solution. Then poly(methyl acrylate) grafted khaya cellulose 1 (5 g) was placed into a two-neck round bottom flask fixed with a stirrer, condenser and thermostat water bath. The prepared hydroxylamine solution was then added into the flask and the reaction was heated at 70 °C for 6 h. The chelating polymeric ligand was separated from hydroxylamine solution by filtration and washed with aqueous methanol. The ligand was treated with 200 mL of 0.1 M HCl (in methanol), filtered and washed several times with methanol and dried at 50 °C to get a constant weight [36].

Preparation of the poly(hydroxamic acid) copper complex 3

A stirred suspension of **2** (2 g) in 50 mL water was added into an aqueous solution of $CuSO_4 \cdot 5H_2O$ (492 mg, in 30 mL H₂O) at room temperature. The blue $CuSO_4$ was immediately turned into green color copper complex ($\emptyset = 17.5 \pm 2$ nm, Fig. 1a) and the mixture was stirred for 2 h at room temperature. The poly(hydroxamic acid) copper complex **3** was filtered and washed several times with excess amount of ammonium chloride, water, MeOH and dried at 60 °C for 2 h. The ICP-AES analysis showed that 0.5 mmol/g of copper [36, 37] was adsorbed by the poly(hydroxamic acid) ligand.

Preparation of the poly(hydroxamic acid) Cu-nanoparticles (CuN@PHA)

Poly(hydroxamic acid) copper complex **3** (500 mg) was dispersed in 50 mL deionized water and hydrazine hydrate (1 mL) was added into the reaction mixture. The resulting reaction mixture was stirred at room temperature for 3 h. The dark brown color **CuN@PHA** ($Ø = 3.2 \pm 1$ nm, Fig. 1c) material was collected by filtration, washed with excess amount of water, methanol and dried under vacuum at 100 °C. The **CuN@PHA** was stored under nitrogen atmosphere [38].

General procedure for Click reaction

A 5-mL glass vessel was charged with **3** (1 mg, 0.05 mol%), alkyne (1 mmol) and aromatic azide (1.1 mmol) in 5 mol% aqueous solution of sodium ascorbate (3 mL). The reaction mixture was stirred at 80 °C for 3 h. The reaction mixture was diluted with EtOAc and the insoluble **3** was recovered by filtration. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were dried over MgSO₄ and

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concentrated under reduced pressure to give the corresponding triazoles. The crude product was purified by silica gel short column chromatography (EtOAc /hexane).

General procedure for Michael addition reaction

In a typical experiment, a mixture of amine (10 mmol), α , β -unsaturated Michael acceptor (11 mmol) and khaya cellulose supported **CuN@PHA** (2 mg, 0.016 mol%) in 10 mL MeOH was stirred at room temperature for 5 h. The reaction progress was monitored by GC analysis. After completion of the reaction, **CuN@PHA** was filtered, washed with MeOH (3 x 5 mL), dried, and reused in the next run under the same reaction conditions. The filtrate was concentrated to give the crude product, which was purified by column chromatography (hexane/ethyl acetate) to give the corresponding Michael addition products.

Results and discussion

The khaya fiber was successively boiled with 17% NaOH and glacial acetic acid respectively. The resulting cellulose was then washed with water and bleached with hydrogen peroxide. The obtained white color cellulose was graft copolymerized with methyl acrylate using ceric ammonium nitrate as an initiator to give cellulose supported poly(methyl acrylate) **1** which was further treated with hydroxylamine provided poly(hydroxamic acid) chelating ligand **2**. The poly(hydroxamic acid) functionalized khaya cellulose was then treated with aqueous solution of $CuSO_4 \cdot 5H_2O$ at room temperature to give green color poly(hydroxamic acid) copper complex **3** (Scheme 1). The ICP-AES analysis revealed that 0.5 mmol/g of copper was adsorbed with the poly(hydroxamic acid) ligand **2**. The copper complex **3** was then treated with hydrazine hydrate [38] to give dark brown color **CuN@PHA** ($\emptyset = 3.2 \pm 1$ nm).

FTIR analysis

The IR spectrum of fresh khaya cellulose showed adsorption bands at 3430 and 2915 cm⁻¹ which referred to O-H and C-H stretching, respectively (Fig. 1, ESI). The band at 1655 cm⁻¹ was due to the bending mode of OH and a smaller peak at 1450 cm⁻¹ was observed for CH₂ symmetric stretching [39]. The absorbance at 1385 and 1162 cm⁻¹ originated from the O-H bending and C-O stretching, respectively. The C-O-C pyranose ring skeletal vibration produced a strong band at 1085 cm⁻¹. A small sharp peak at 908 cm⁻¹ corresponded to the glycosidic C₁-H deformation with ring vibration contribution and OH bending indicating α -glycosidic linkages between glucose units in cellulose [39]. The IR spectrum of poly(methyl acrylate) grafted cellulose 1 showed new absorption bands at 1742, 1475, 1402 cm⁻¹ due to C=O, scissoring and wagging stretching of methyl group respectively [40]. The peak at 2980 and 2870 cm⁻¹ represent C-H (sp³) stretching of methyl group. The poly(hydroxamic acid) 2 showed new absorption bands at 1690 and 1651 cm⁻¹ corresponding to the C=O stretching and N-H bending modes. Additionally, a new broad band at 3185 $\rm cm^{\text{-1}}$ for N-H stretching and 1410 cm⁻¹ for OH bending were observed.



Scheme 1. Preparation of the copper complex 3.

It was found that the C=O band at 1742 cm⁻¹ in **1** shifted to 1690 cm⁻¹ which confirmed the successful production of hydroxamic acid ligand onto the khaya cellulose. The C=O stretching band of hydroxamic acid was found at 1738 cm⁻¹ after its complexation with Cu(II) [41]. New peaks at 1618, 1450 and 1162 cm⁻¹ were assigned for C=N and C-O stretching respectively. A peak at 615 cm⁻¹ further confirmed the successful incorporation of copper with the poly(hydroxamic acid) ligand **2** [41b].

3

FESEM, HRTEM, XPS and XRD analysis

The green color photo image showed copper complex **3** (Fig. 1a), which was turned into light yellow (Fig. 1b) when treated with sodium ascorbate in Click reaction and dark brown color (Fig. 1c), **CuN@PHA** for Michael addition was obtained by the reduction of **3** with hydrazine hydrate.



Fig. 1 (a) Photo image of copper complex 3, (b) after reduction of 3 using sodium ascorbate and (c) after reduction of 3 using hydrazine hydrate.

The FESEM micrograph of khaya cellulose showed stick like morphology (Fig. 2a) whereas poly(methyl acrylate) grafted

DOI: 10.1039/C6RA08155J

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cellulose **1** showed distinguishable surface of wooden stick like cellulosic structure having rough surface surrounding onto the stick (Fig. 2b). The poly(hydroxamic acid) chelating ligand **2** exhibited distinct spherical morphology (Fig. 2c) indicating the successful hydroximation of **1**. The SEM image of **3** displayed bigger spherical morphology which revealed that ligand **2** was aggregated due to the cross linkage between poly(hydroxamic acid) chelating ligands and Cu(II) (Fig. 2d).



Fig. 2 (a) SEM image of khaya cellulose, (b) SEM image of 1, (c) SEM image of 2, and (d) SEM image of 3, (e) TEM image of copper complex 3, (f) TEM images of CUN@PHA.

The TEM analysis of **3** showed in presence of Cu(II) onto the cellulose surface (Fig. 2e) and the average particles size $\phi = 17.5 \pm 2$ nm was measured. The TEM image of **CuN@PHA** demonstrated the well dispersion of smaller size distribution (Fig. 3) of copper nanoparticles ($\phi = 3.2 \pm 1$ nm) onto the cellulose backbone (Fig. 2f). The XPS spectrum of copper complex **3** and **CuN@PHA** were showed (Fig. 4) a single Cu 2p3/2 peak at 934.5 and 931.9 eV which are assigned for the binding energy of Cu(II) and Cu(0) respectively [15c, 23, 38]. Additionally, an UV-vis spectrum of **CuN@PHA** exhibited a single absorption at 694 nm (Fig. 2, ESI) that was assigned for Cu-N coordination [15c]. The X-ray diffraction (XRD) analysis of **CuN@PHA** confirmed the formation of metallic copper nanoparticles in Bragg's reflections at 2 $\theta = 43.6$, 50.5, and 74.5, which can be indexed as the (111), (200), and (220) planes of copper (Fig. 5) [42].



Fig. 3 Size distribution of the CuN@PHA. The sizes were determined for 100 nanoparticles selected randomly.



Fig. 4 XPS image of 3 and CuN@PHA



Fig. 5 XRD pattern of CuN@PHA.

Copper catalyzed Click reaction

The khaya cellulose supported poly(amidoxime) copper complex **3** was used in the investigation for Click reaction of benzyl azide (**5a**) and phenylacetylene (**4a**). The initial reaction was carried out using 1 mol% of **3** at 50 °C for 2 h in the presence of 5 mol% aqueous solution of sodium ascorbate and was found to afford smoothly the desired product, **6a** in 92% yield (Table 1, entry 1). Whereas, 94% and 90% yields were obtained when the same reactions were performed using 0.5 and 0.1 mol% of **3** (entries 2, 3). We also

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accomplished the reaction by changing of catalyst loading, temperature (entries 4-6) and eventually found that 0.05 mol% of **3** would be enough to promote this reaction efficiently (entry 4).



$(1 \text{ purel}) = (1 \text{ for } 1 \text$								
(1111101) 4a	(1.1 mmol) 5a		6a					
Entry	Cat (mol%)	Temp (∘C)	Time (h)	Yield (%)				
1	1	50	2	92				
2	0.5	50	4.5	94				
3	0.1	50	7	90				
4	0.05	80	3	96				
5	0.01	90	6	89				
6	0.05	90	2.5	92				

^aReactions were carried out using 1 mmol of phehylacetylene, 1.1 mmol of benzyl azide, catalytic amount of **3** in 5 mol% of aqueous sodium ascorbate.

To explore the board applicability of **3** in the Click reaction with various alkynes and azides were investigated under earlier settled optimized reaction conditions and the results are summarized in Table 2. When the cyclization of phenylacetylene (**4a**) and 4-methylbenzyl azide (**5b**) was carried out with **3** in presence of 5 mol% sodium ascorbate at 80 °C for 3 h, **3** drove the reaction smoothly to afford triazole **6b** in 95% yield. The sodium ascorbate reduced Cu(II) to Cu(I) and the color of **3** was changed from green to yellow during the reaction progress (Fig. 1b).

Table 2. Click reaction of organic azides and alkynes^a



^aReactions were carried out using 1 mmol of alkyne, 1.1 mmol of organic azide, 0.05 mol% of **3** in 5 mol% of aqueous sodium ascorbate at 80 °C for 3 h.

The 4-tolylacetylene (**4b**) react with benzyl azide (**5a**) and 1-azido-2phenylethane (**5c**) efficiently under similar reaction conditions to provide the corresponding triazoles **6c** and **6d** in 93% and 91% yield respectively. It should be noted that an aliphatic hex-5-yn-1-ol (**4c**), readily reacted with a variety of benzyl and naphthyl azides to give the corresponding triazoles **6e-g** in 88-90% yields. The copper complex **3** also promoted the reaction of cyclic alkynes bearing tertiary alcohol **4d**, acetal **4e** and amine moieties **4f** with benzyl azide (**5a**) to give the corresponding products **6h-j** in 89-91% yields. Interestingly, our copper complex **3** did not affect the alcohol, acetal, and amine groups. Thus, **3** can be used in the wide range of substances.

CuN@PHA catalyzed Michael addition reaction

Being inspired by the successful application of 3 in Click reaction, Michael addition reaction of amines and α , β -unsaturated compounds was considered to find the catalytic versatility of the prepared khaya cellulose supported Cu-catalyst. The addition reaction between piperidine and butyl acrylate was taken as a model reaction at room temperature to evaluate the optimum condition for high catalytic performance of CuN@PHA. Table 3 present the results of the effect of catalyst dosages and reaction time. The initial reaction was carried out using piperidine (7a) and butyl acrylate (8a) in the presence of 0.16 mol% of (32 mg) CuN@PHA which efficiently promoted the reaction to give the corresponding addition product 9a in 94% yield within 1 h (Table 3, entry 1). When 0.08 mol% of CuN@PHA was used, the reaction time was increased as expected and it was raised to 2 h, (entry 2). When the loading of CuN@PHA is further decreased (0.032 to 0.016 mol%), it took little longer time to complete the reaction (entries 3, 4). The catalyst loading was again decreased to 0.008 mol% (1 mg) which also effectively forwarded the addition reaction (entry 5). It is interesting to notice that the Michael addition reaction was also promoted when 2 and 3 were used as a catalyst which provided only 11 and 17% yield of 9a respectively (entries 6, 7).

Table 3. Optimization of Michael addition reaction^a

NH + CO ₂ Bu CuN@PHA MeOH, rt									
	7a	8a		9a					
Entry	Catalyst	Mol%	Time (h)	TON	TOF (h ⁻¹)	Yield (%)			
1		0.16	1	587	587	94			
2	CUNEDUA	0.08	2	1150	575	92			
3	CUN@PHA	0.032	4	2812	703	90			
4		0.016	5	5687	1137	91			
5		0.008	6	10875	1812	87			
6	2	(1 mg)	5	-	-	11			
7	3	(1 mg)	5	-	-	17			

^aReactions were carried out using 10 mmol of piperidine, 11 mmol of butyl acrylate in 10 mL MeOH at room temperature.

However, the TON and TOF calculation of the catalyst showed the highest value when 0.008 mol% **CuN@PHA** was used (entry 5). As far our knowledge, these are the highest TON and TOF obtained for cellulose supported copper nanoparitcles catalyzed Michael addition reaction.

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Having the optimised conditions in hand, we investigated the wide applicability of **CuN@PHA** in Michael addition reaction (Table 4). The five membered cyclic pyrolidine (**7b**) and sterically hinderd dibenzyl amine (**7c**) (10 mmol) underwent Michael addition reaction with butyl acrylate (**8a**) (11 mmol) in the presence of 0.016 mol% (2 mg) of **CuN@PHA** at room temperature in methanol to afford *N*-alkylated products **9b**, **9c** in 91% and 95% yield respectively. The addition reaction of dibenzyl amine (**7c**) and acrylonitrile (**8b**) was efficiently forwarded to **9d** in 92% yield. The **CuN@PHA** also fosterd the Michael addition reaction of methyl acrylate (**8c**) with piperidine (**7a**), dibutylamine (**7d**) and morpohline (**7e**) smoothly affroded the corresponding products **9e-g** in up to 95% yield. Thus, it is observed that **CuN@PHA** effectively explored Michael addition reaction with both open chain and cyclic secondary amines.



^aReactions were carried out using 10 mmol of amine, 11 mmol of Michael acceptor, 0.016 mol% of **CuN@PHA** in 10 mL MeOH at room temperature for 5 h.

In addition, it is important to note that primary aliphatic amine, ethylenediamine (**7f**) also efficiently took part in the Michael addition reaction with **8a** and **8b** giving poly-alkylated products **9h** and **9i** in 88% and 87% yield respectively. Recently, R K. Reddy et al. [23] reported that, microcrystalline cellulose supported Cunanoparticles catalyzed Aza-Michael reaction of primary and secondary amines. In their report, they used 3.6 mol% of the copper nanoparticles and obtained similar results. Whereas, we used only 0.016 mol% of the **CuN@PHA** which is 225 times lower catalytic loading compare to their report.

Recycling of copper complex 3 and CuN@PHA

Considering the importance of reusability of the catalyst in heterogeneous catalysis system, we concentrated recycling our copper complex **3** and **CuN@PHA** and the results are shown in Fig. 6. After completion of the first run, the reaction mixture was filtrated and the catalyst was washed with ethyl acetate/methanol. The solid catalysts were dried at 80 °C under vacuum and then used it in the next run without changing the reaction conditions. The copper complex **3** and **CuN@PHA** were observed to work upto six times without significant loss of its catalytic activity. The only negligible loss of catalytic activity was found under the same reaction conditions as for initial run. The small reduction of catalytic

activity was noticed after five cycles owing to the loss of **CuN@PHA** during the filtration process. Only for Click reaction, ICP-AES analysis showed that a trace amount of copper species (<0.13 mol ppm of Cu) was washed out into the reaction mixture after five consecutive runs. Therefore, it can be rationally believed that our prepared catalysts can be recycled as well as reused repeatedly for large scale production with no significant loss of its catalytic activity.



Fig. 6 Recycling of the copper complex 3 and CuN@PHA

Chemoselectivity test of Aza-Michael reaction

We further explored the chemo selectivity of **CuN@PHA** in *N*-alkylation reaction, which is important in the synthetic applications. For this, a mixture of 4-methylaniline and morpholine were exposed with methyl acrylate (4 mol equiv) according to the Table 4. It is very interesting to note that 4-methylaniline did not undergo the reaction whereas only mono Michael adduct of morpholine **9g** was produced exclusively. This obviously indicated the chemo selectivity of aliphatic amines versus aromatic amines towards the catalyst **CuN@PHA** and this is due to the less reactivity of aromatic amines compared to aliphatic amines.



Scheme 2. Chemo selectivity of Michael addition reaction

Hot filtration test of the Click reaction

The heterogeneity of the supported catalyst in the reaction medium is another vital issue. We performed hot filtration experiment to check whether the catalytic reaction proceeded through heterogeneous condition or not (Fig. 7). Thus, we carried out Click reaction of benzyl azide and phenylacetylene according to Table 2. The reaction was performed for one hour under the identical condition and then the reaction mixture was filtrated at hot condition and the filtrate was further heated under the identical reaction conditions and observed no reaction was further preceded at all. The ICP-AES analysis of filtrate revealed that no copper species was latched out into the aqueous solution. Thus, it is Published on 06 June 2016. Downloaded by University of Sussex on 07/06/2016 09:41:09

realized that the coupling reaction was forwarded under heterogeneous conditions.



Fig 7. Hot filtration of Click reaction

Conclusions

In summary, we have synthesized khaya cellulose supported poly(hydroxamic acid) copper complex and copper nanoparticles and successfully applied in the Click and Michael addition reactions of organic azide with terminal alkynes and aliphatic amines with α,β -unsaturated Michael acceptors respectively. The catalysts efficiently (0.05 to 0.008 mol%) promoted C-N bond formation reaction to produce their corresponding products with excellent yields as well as exhibited magnificent reusability without any significant degradation of its reactivity for several cycles, promising a reusable environment-friendly catalyst for practical applications.

Acknowledgements

This work is supported by Ministry of Education Malaysia, fund no. RDU 140124 and RDU 140343. Authors are grateful to Nor Hafizah Bt Zainal Abidin, scientific officer, and central lab, University Malaysia Pahang.

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Graphical Abstract:

