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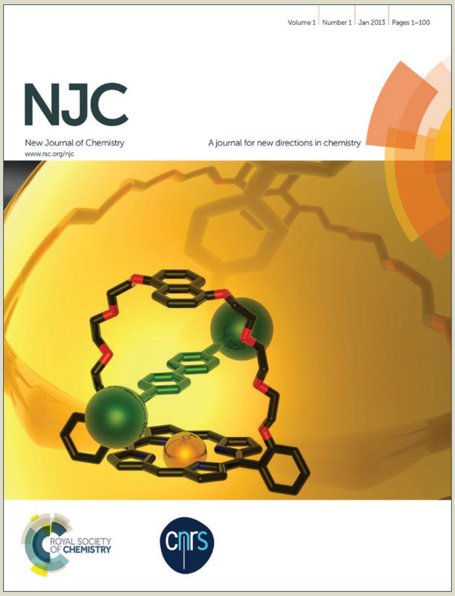

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ARTICLE

Waste Corn-cob Cellulose Supported Bio-Heterogeneous Copper Nanoparticles for Aza-Michael Reactions

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Bio-heterogeneous poly(amidoxime) copper nanoparticle was prepared onto the modified surface of waste corn-cob cellulose through graft copolymerization process. The Cu-nanoparticle (0.05 mol% to 50 mol ppm) was selectively promoted Aza-Michael reaction of aliphatic amines to give the corresponding alkylated products at room temperature in methanol. The supported nanoparticle was easy to recover and reused eight times without significance loss of its activity.

Keywords: Amine, Aza-Michael reaction, Corn-cob, Cellulose, Copper nanoparticles.

1. Introduction

Conjugate reaction of various amines with α, β-unsaturated carbonyl compounds provides β-amino carbonyl ingredients, which have attracted great attention to the synthesis of biological active molecules and some essential intermediate of antibiotics and pharmaceutical products [1-6]. The conjugate addition of amines to α, β-unsaturated compounds, which is known as atom economic Aza-Michael reaction and very simple to carry out. Generally, Aza-Michael addition is proceeded in presence of strong acid or bases and some side products are formed. Thus, chemists have paid more attentions to the development of more mild catalytic systems. A number of homogeneous catalyzed Aza-Michael reaction such as $AlCl_3$ [7], $PtCl_4{\cdot}5H_2O$ [8], $InCl_3$/TMSCl [9], $Bi(NO)_3$ [10] samarium iodobinaphtholate [11] boric acid [12], $[Ni(PPP)(THF)](ClO_4)_2$ [13], Pd(*N*,*N′*-ppo)Cl_2 [14], and ionic liquids [15-18], TMSCl-promoted transition metal [19] have been reported. Since the loss of material and difficulty of purification in each step reaction will also dramatically reduce the overall efficiency of a synthetic process. Thus, not only the catalytic activity and selectivity but also the stability and reusability for safe, non-toxic, sustainable chemistry, and green organic synthesis, development of heterogeneous metal catalysts become a particular interest. Therefore, to devise a perfect heterogeneous metal catalyst that matches the reactivity, selectivity, broad applicability and reusability of the catalyst would be highly acceptable. In this context, a lot of heterogeneous metal catalysts are employed. For instant MOF-99 [20] polystyrene supported CuI-imidazole complex [21] biomaterial supported organo-catalyst [22] silica sulfuric acid [23] phosphate impregnated titania [24] nanocrystalline copper(II) oxide [25], PANI-Cu [26] PANI-In [27], PSSA [28], Amberlyst-15 [29], cellulose-Cu(0) [30], $CeCl_3{\cdot}7H_2O/NaI/Al_2O_3$ [31], polystyrene-$AlCl_3$ [32], enzymes [33, 34] showed good catalytic activity for the Michael additions. Although many economic and sustainable protocols have been employed by the researchers dedicated to the development of green processes for Aza-Michael additions, some of catalysts have poor or even weak catalytic effect [35-37].

Recently, scientists are searching cheap and more environmentally friendly sustainable resources and processes. In this connection, cellulose would be the most acceptable material, which is widely abundant in nature. Develop of bio-based materials and composites could be a promising solution both in terms of environmental and performances aspects. The structure of biopolymers provides several advantages such as low density and cost, bio-renewable character, ubiquitous availability and their interesting mechanical properties compared with glass fibres [38]. Thus, natural celluloses would be highly desirable attractive candidates to explore the solid support of catalysts [39]. Cellulose has interesting features for example, high sorption capacity, stability and physical and chemical versatility makes them attractive to use as supports. Cellulose can be chemically modified and effective chelating ligands can be introduced onto the cellulose backbone [40, 41]. Recently, several biopolymers, for example alginate [42], gelatin [43], starch [44] and chitosan [45] derivatives have been utilized as supports for catalytic applications. Thus, development of a general, simple and convenient method, which can be applied to a number of substrates of different natures in a catalytic process under milder and environmentally friendly conditions, is highly desirable. Recently, we developed waste corn-cob cellulose supported poly(amidoxime) ligand which successfully absorbed a lot of metal complexes from the industrial waste water [46].

Herein we report corn-cob cellulose supported poly(amidoxime) copper nanoparticles (**CuN@PA**) catalyzed regioselective Aza-Michael reaction of aliphatic amines with α, β-unsaturated compounds in methanol at room temperature. The **CuN@PA** showed high efficiency (0.05 mol% to 50 mol ppm) and it was reused several times without significance loss of catalytic activity.

2. Experimental

2.1 General Information

All manipulations were performed under atmospheric conditions 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. $CuSO_4{\cdot}5H_2O$ was purchased from Aldrich Chemical Industries, Ltd. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra were measured with a BRUKER-500 spectrometer, central laboratory, University Malaysia Pahang. The ^{1}H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts were reported relative to $CDCl_3$ (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 an ESCALA 250 (Thermo Fisher Scientific K.K.) by Hi-Tech Instruments SDN BHD, Puchong, Malaysia. FE-SEM was measure with JSM-7800F, central laboratory, University Malaysia Pahang. TEM was measure 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).

2.2 Materials

The waste corn-cob was obtained from Gambang, Pahang, Malaysia. Corn-cobs were cut into small size (3 cm long average). The raw corn-cob (100 g) was boiled with 10% NaOH (800 mL), glacial acetic acid (800 mL) for 4 h and 2 h respectively, and washed with distilled water. The raw corn-cob cellulose was bleached with hydrogen peroxide (500 mL) and 5% NaOH (300 mL), washed with distilled water (500 mL) several times and oven dried at 50 °C before use. Acrylonitrile monomer purchased from Aldrich and monomer was passed through the columns filled with chromatographic grade activated alumina to remove the inhibitor. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich), methanol (Merck), and other analytical grade reagents were used without purification.

2.3 Graft copolymerization

The graft copolymerization reaction was carried out in 1 L three-neck round bottom flask equipped with stirrer and condenser in thermostat water bath. The cellulose slurry was prepared by stirring 6 g of corn-cob cellulose in 150 mL distilled water for overnight. The N_2 gas was purged into the flask to remove oxygen during the grafting process. The slurry was heated to 55 °C and 2.17 mL of diluted sulphuric acid (H_2SO_4/H_2O, 1:1) was added to the mixture. After 5 min, 2 g of CAN (in 10 mL solution) was added and the reaction mixture was stirred continuously. After 20 minutes, 14 mL of acrylonitrile monomer was added into the cellulose suspension and stirred for 4 h under nitrogen atmosphere. The reaction mixture was cold and the obtained cellulose was washed several times with aqueous methanol (methanol/water, 4:1). The product was finally oven dried at 50 °C to obtain a constant weight [47].

2.4 Synthesis of poly(amidoxime) ligand 1

Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) 20 g was dissolved in 500 mL of aqueous methanol (methanol/water, 4:1) and neutralized by NaOH solution and the resulting NaCl precipitate was removed by filtration. The pH of the reaction was adjusted to pH 11 by adding of NaOH solution. The ratio of methanol and water was maintained as 4:1 (v/v). Poly(acrylonitrile) grafted corn-cob cellulose 10 g was placed into a two-neck round bottom flask equipped with a stirrer, condenser and thermostat water bath. The hydroxylamine solution was then added to the flask and the reaction was starred at 70 °C for 4 h. After completion of reaction, the chelating ligands were separated from the hydroxylamine solution by filtration followed by washed with aqueous methanol. The obtained cellulose based amidoxime ligand was neutralized with 100 mL of methanolic 0.1 M HCl solution. The ligand was filtered and washed several time with aqueous methanol and dried at 50 °C for 6 h [48, 49].

2.5 Preparation of the poly(amidoxime)copper complex 2

An aqueous solution of $CuSO_4{\cdot}5H_2O$ (126 mg, in 5 mL H_2O) was added into a stirred mixture of 1 g of poly(amidoxime) ligand **1** in 25 mL water at room temperature. The blue $CuSO_4$ was immediately turned into green colour and the mixture was stirred for 1 h at room temperature. The reaction mixture was filtrate and washed several times with excess amount of water, MeOH and dried at 60 °C for 1 h. The ICP-AES analysis showed that 0.5 mmol/g of copper [49] was coordinate with the poly(amidoxime) ligand.

2.6 Preparation of the poly(amidoxime) Cu-nanoparticles (CuN@PA)

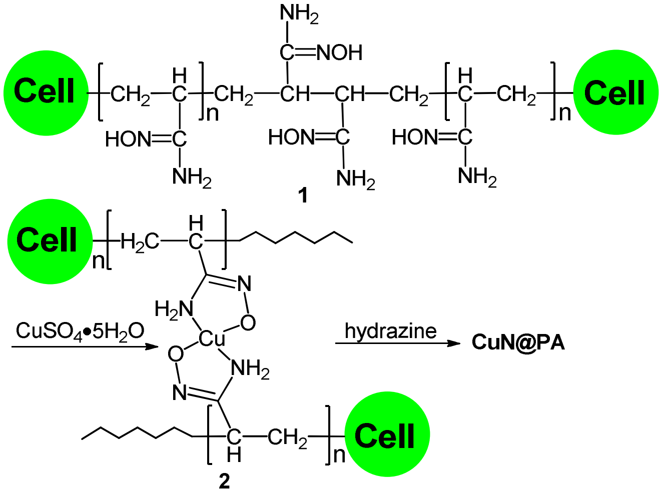
Poly(amidoxime)copper complex **2** (500 mg) was dispersed in 50 mL deionized water and then hydrazine hydrate 0.7 mL was added. The resulting dark brown color **CuN@PA** materials were collected by centrifugation, washed with methanol, acetone, and dried under vacuum at 100 °C and stored under nitrogen atmosphere.

2.7 General procedure for Aza-Michael reaction

In a typical experiment, a mixture of amine (1 mmol), α, β-unsaturated Michael acceptor (1.1-4 mmol), corn-cob cellulose supported **CuN@PA** (0.05 mol%) in 2 mL MeOH was stirred at room temperature for 1 h. The reaction progress was monitored by TLC analysis. After completion of the reaction, **CuN@PA** 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.

3. Results and discussion

The waste corn-cob was obtained from Gambang, Pahang, Malaysia.



Scheme 1. Synthesis of waste corn-cob cellulose-supported **CuN@PA**.

The waste corn-cobs were cut into small pieces and successively boiled with 10% NaOH and glacial acetic acid for 4 h and 2 h respectively. The resulting cellulose was washed with water and bleached with hydrogen peroxide and 5% NaOH respectively. The obtained white colour cellulose was graft polymerized with acrylonitrile using ceric ammonium nitrate as a redox initiator to give cellulose supported poly(acrylonitrile) which was further reacted with hydroxylamine provided poly(amidoxime) chelating ligand **1** (Scheme 1).

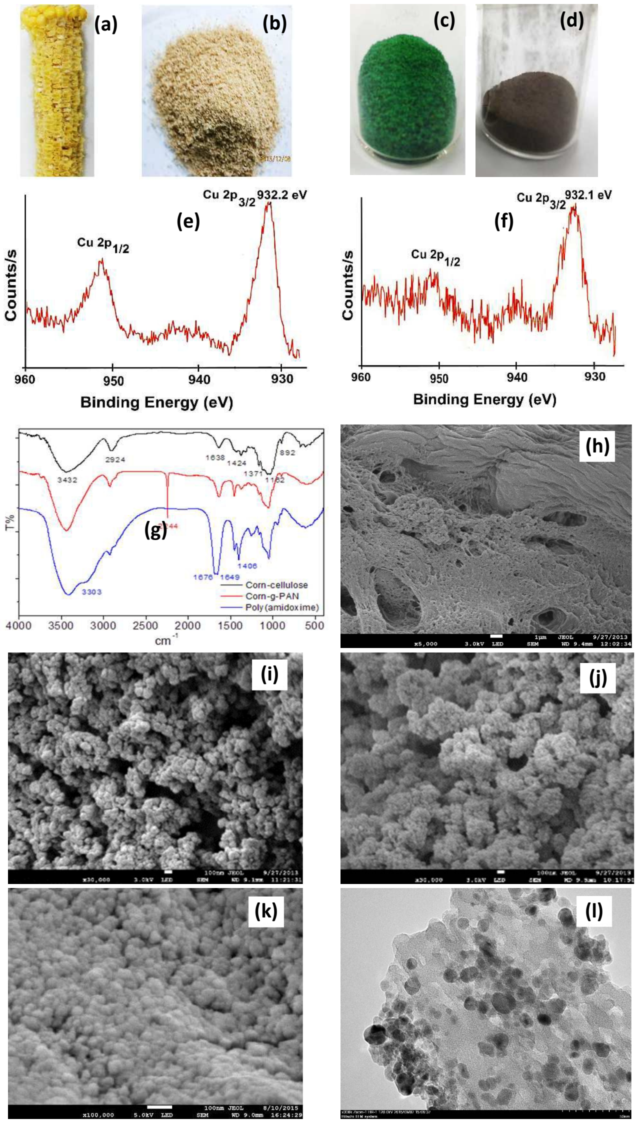
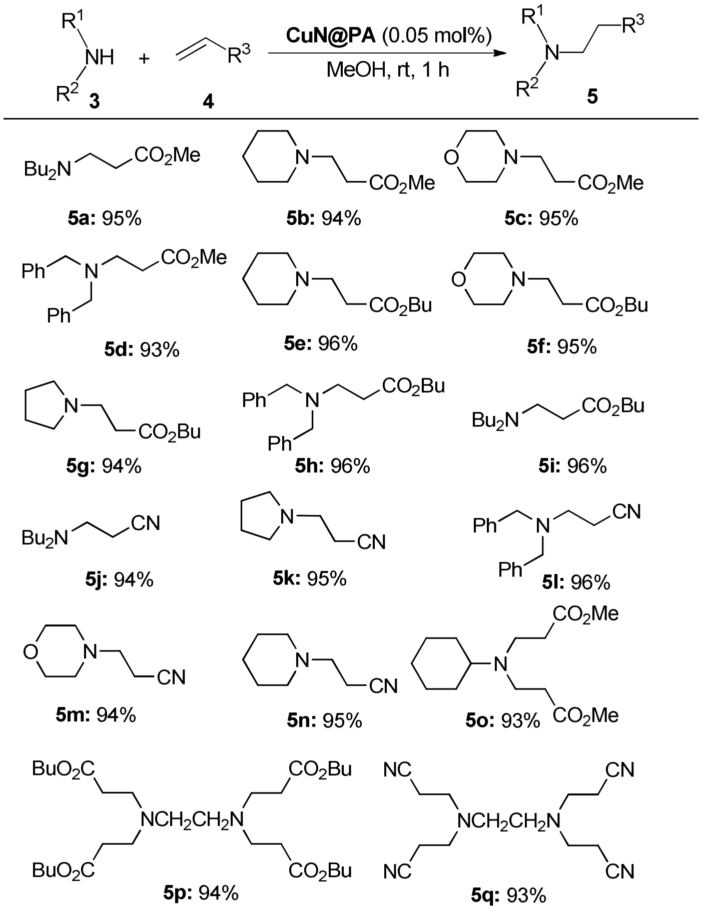


Fig 1. (a) Photo image of waste corn-cob, (b) Photo image of **1**, (c) Photo image of **2**, (d) Photo image of **CuN@PA**, (e) XPS of **CuN@PA**, (f) XPS of used **CuN@PA**, (g) IR spectrum of cellulose and modified cellulose, (h-k) SEM images of cellulose, cellulose supported poly(acrylonitrile), **1**, and copper complex **2** respectively, (l) TEM image of **CuN@PA**.

Figures 1a-d are showing the photographic images of waste corn-cob, corn-cob cellulose, poly(amidoxime) copper complex **2**, and **CuN@PA** respectively. The IR spectrum of cellulose showed the absorption bands at 3432 cm^{-1} and 2924 cm^{-1} for O-H and C-H stretching, respectively (Fig. 1g). A small peak at 1424 cm^{-1} belongs to the CH_2 symmetric stretching [50]. A small peak at 1371 and a broad band at 1162 cm^{-1} showed for C-O stretching. The C-O-C pyranose ring skeletal vibration gives a strong band at 1062 cm^{-1}. A small sharp peak at 892cm^{-1} corresponds to the glycosidic C_1-H deformation with ring vibration contribution and OH bending, which is characteristic of α-glycosidic linkages between glucose in cellulose [46, 48]. The IR spectrum of acrylonitrile-grafted cellulose exhibited a new absorption band at 2244 cm^{-1} attributed to the CN stretching of nitrile.

The poly(amidoxime) chelating ligand showed new absorption bands at 1676 and 1649 cm^{-1} correspond to the C=N stretching and N-H bending modes, respectively. In addition, a shoulder created at 3303 cm^{-1} for N-H and OH stretching bands and 1406 cm^{-1} for bending. A clear evidence for the CN band for 2244 cm^{-1} was disappeared and a new absorption bands for amidoxime group was appeared, which confirmed the successful production of poly(amidoxime) function onto the cron-cob cellulose grafted copolymers. The poly(amidoxime) function was then treated with aqueous copper sulphate at room temperature to give blue colour poly(amidoxime) copper complex **2** (Fig. 1c). The IR of **2** showed at 3303 cm^{-1} and 1125 cm^{-1} [51], which indicated the copper salt was coordinate with the poly(amidoxime) ligand **2**. The copper complex **2** was then treated with hydrazine hydrate [52] to give dark brown colour copper nanoparticles **CuN@PA** (Ø = 8.0 ± 7 nm) which were stabilized by the poly(amidoxime) ligands (Fig. 1d and 1l).

Table 1. Aza-Michael addition reaction of amines[a]



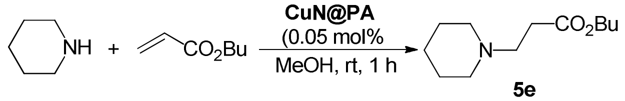
[a]Reactions were carried out using 1 mmol of amine, 1.1 mol equiv of Michael acceptor, 0.05 mol% of **CuN@PA** in 2 mL MeOH at room temperature for 1 h.

The XPS spectrum showed (Fig. 1e) a single Cu 2p3/2 peak at 932.2 eV, which is assigned for the binding energy of Cu(0) [52]. The FE-SEM micrograph of the corn-cob cellulose showed unsmooth morphologies including fine crystalline surface (Fig. 1h). The FE-SEM micrograph of the poly(acrylonitrile) grafted corn-cob cellulose showed spherical shape beads structure which is distinguishable surface (Fig. 1h) of corn-cob cellulosic fine crystalline structure and it is clear evidence for grafting occurred on the cellulosic materials (Fig. 1i). The poly(amidoxime) chelating ligand **1** showed distinct morphologies with finest beads structure looks small gain like structure (Fig. 1j). The SEM micrograph of poly(amidoxime) ligand after adsorption of $CuSO_4$ is compact surface (Fig. 1k), which is different with finest beads structure of **1** (Fig. 1j). The TEM image showed the well dispersion of copper nanoparticles on to the cellulose surface (Fig. 1k).

To check the reactivity of **CuN@PA** we applied this corn-cob cellulose supported copper-nanoparticles **CuN@PA** to the conjugate addition of aliphatic amines with different Michael acceptors at room temperature and the results are summarized in Table 1. The cellulose supported copper nanoparticles **CuN@PA** was efficiently (0.05 mol%) promoted Aza-Michael reaction in methanol at room temperature. The α, β-unsaturated carbonyl Michael acceptor, methyl acrylate was smoothly promoted the Aza-Michael reaction with secondary aliphatic amine such as dibutylamine, piperidine, morpohline and sterically hindered secondary dibenzylamine to give the corresponding products in up to 95% yields (**5a-d**). Similarly, butyl acrylate was efficiently provided the corresponding Michael addition adducts in up to 96% yields (**5e-i**). The α, β-unsaturated acrylonitrile was also promoted the addition reaction to give the mono alkylated products (**5j-n**). It should be noted that, cyclohexylamine and ethylenediamines ware also efficiently underwent the Aza-Michael reaction to give poly alkylated products **5o-q** with methyl, butyl acrylate and acrylonitrile Michael acceptor respectively.

The recycling of the catalyst is an important issue in heterogeneous catalysis system. Again, we turn our attention to reuse our cellulose supported copper nanoparticles **CuN@PA** and the results are summarized in Table 2. After competition of the first run, the reaction mixture was filtrated and washed with methanol. The XPS image (Fig. 1f) of reused **CuN@PA** showed similarity with the fresh **CuN@PA** (Fig. 1e). The solid brown colour **CuN@PA** was dried at 80 °C under vacuum, and then used it in the next run without changing of the reaction conditions.

Table 2. Aza-Michael reaction by recycled catalyst **CuN@PA**[a]



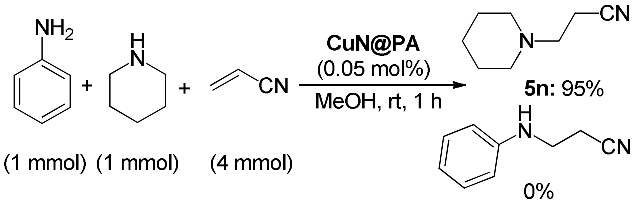
5e

Cycle	Yield (%)[a]	Cycle	Yield (%)[a]
1	96	6	93
2	94	7	92
3	94	8	91
4	93		
5	94 (<0.11 mol ppm Cu was leached out)		

[a] Reaction was carried out using 1 mmol of piperidine, 1.1 mmol of butyl acrylate, 0.05% of **CuN@PA** in 2 mL of MeOH at room temperature.

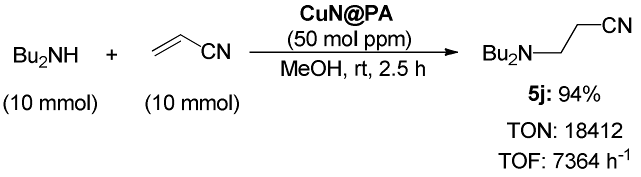
The **CuN@PA** could be used eight times without significance loss of catalytic activity. Only slight loss of catalytic activity was observed under the same reaction conditions as for initial run. The slight loss of catalyst activity was observed after five cycles due to the loss of **CuN@PA** during the filtration process. A trace amount of copper species (<0.11 mol ppm of Cu, ICP-AES) was leached out from the reaction mixture. Thus, it is reasonable to believe that the cellulose supported copper catalyst can be repeatedly used for large-scale production without significant loss of its catalytic activity.

The chemoselectivity of **CuN@PA** was then investigated. Thus, a mixture of aniline and piperidine were exposed to acrylonitrile (4 mol equiv) under the present reaction conditions (Scheme 2). Interestingly, aniline was not underwent the reaction only the mono Michael adduct of piperidine was obtained exclusively. It is clearly reflects the chemoselectivity of aliphatic amines versus aromatic amines. This selectivity is due the less reactivity of aromatic amines in comparison to aliphatic amines. This selectivity could be useful to discriminate the two types of amines for synthetic applications.



Scheme 2. Chemoselective Aza-Michael reaction.

To investigate the highest catalytic activity obtainable for the Aza-Michael reaction was also performed (Scheme 3). The Michael addition reaction was carried out using 10 mmol of dibutyl amine and acrylonitrile in presence of 50 mol ppm (0.1 mg) of **CuN@PA** which was still efficiently promoted the Aza-Michael reaction to provide **5j** in 94% yield. The TON and the turnover frequency (TOF) of the catalyst reached 18412 and 7364 h^{-1}, respectively; these are, as far as we know, the highest TON and TOF obtained for a cellulose supported **CuN@PA** catalysed Aza-Michael reaction.



Scheme 3. Lower catalytic loading (50 ppm) in the Aza-Michael reaction.

Conclusion

In summary, the waste corn-cob cellulose supported poly(amidoxime) copper-nanoparticle was efficiently promoted chemoselective Aza-Michael addition of aliphatic amines with conjugate α, β-unsaturated Micheal acceptors. The addition reactions were efficiently (0.05 mol% to 50 mol ppm) promoted to provide the corresponding products with excellent yields. After completion of the reaction, supported nanoparticle was separated from the reaction mixture by simple filtration, and it was reused several times without significance loss of activity.

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Notes and references

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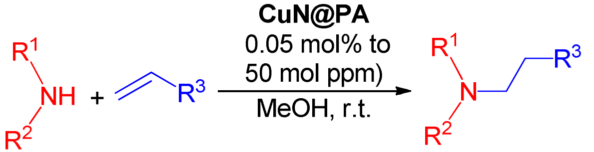
1 G. Bartoli, C. Cimarelli, E. Marcantoni, G. Palmieri, Petrini, M. *J. Org. Chem.* 1994, **59**, 5328.
2 G. Cardillo, C. Tomasini, *Chem. Soc. Rev.* 1996, **25**, 117.
3 A. K. Nezhad, M. N. S. Rad, G. H. Hakimelahi, B. Mokhtari, *Tetrahedron,* 2002, **58**, 10341.
4 S. Fustero, B. Pina, E. Salavert, A. Navarro, M. C. Ramirez de Arellano, A. S. Fuentes, *J. Org. Chem.* 2002, **67**, 4667.
5 P. Traxler, U. Trinks, E. Buchdunger, H. Mett, T. Meyer, M. Mueller, U. Regenass, J. Rosel, N. Lydon, *J. Med. Chem.* 1995, **38**, 2441.
6 A. Graul, J. Castaner, *Drugs Future,* 1997, **22**, 956.
7 W. E. Hahn, W. Szalecki, W. Boszczyk, *Pol. J. Chem.* 1978, **52**, 2497.
8 S. Kobayashi, K. Kakumoto, M. Sugiura, *Org. Lett.* 2002, **4**, 1319.
9 L. Yang, L. W. Xu, C. G. Xia, *Tetrahedron Lett*. 2007, **48**, 1599.
10 N. Srivastava, B. K. Banik, *J. Org. Chem*. 2003, **68**, 2109.
11 D. Didier, A. Meddour, S. B. Lafollee, J. Collin, *Eur. J. Org. Chem.* 2011, 2678.
12 M. K. Chaudhuri, S. Hussain, M. L. Kantam, B. Neelima, *Tetrahedron Lett.* 2005, **46**, 8329.
13 L. Fadini, A. Togni, *Chem. Commun*. 2003, 30.
14 G. A. Ardizzoia, S. Brenna, B. Therrien, *Dalton Trans.* 2012, **41**, 783.
15 S. R. Roy, A. K. Chakraborti, *Org. Lett.* 2010, **12**, 3866.
16 J. M. Xu, Q. Wu, Q. Y. Zhang, F. Zhang, X.-F. Lin, *Eur. J. Org. Chem.* 2007, 1798.
17 X. Chen, X. Li, H. Song, Y. Qian, F. Wang, *Tetrahedron Lett*. 2011, **52**, 3588.
18 L.-W. Xu, J.-W. Li, S.-L. Zhou, C.-G. Xia, *New. J. Chem.* 2004, **28**, 183.
19 18 L.-W. Xu, C.-G. Xia, Synthesis, 2004, 2191.
20 L. T. L. Nguyen, T. T. Nguyen, K. D. Nguyen, N. T. S. Phan, *Appl. Catal. A,* 2012, **42**5, 44.
21 L. Li, Z. Liu, Q. Ling, X. Xing, *J. Mol. Catal. A: Chem.* 2012, **353**, 178.
22 S. Verma, S. L. Jain, B. Sain, *Org. Biomol. Chem.* 2011, **9**, 2314.
23 Y. Wang, Y. Q. Yuan, S. R. Guo, *Molecules,* 2009, **14**, 4779.
24 J. Nath, M. K. Chaudhuri, *Catal. Lett.* 2009, **133**, 388.
25 M. L. Kantam, S. Laha, J. Yadav, S. Jha, *Tetrahedron Lett.* 2009, **50**, 4467.
26 M. L. Kantam, M. Roy, S. Roy, B. Sreedhar, R. L. De, *Catal. Commun.* 2008, **9**, 2226.
27 M. L. Kantam, M. Roy, S. Roy, M. S. Subhas, B. Sreedhar, B. M. Choudary, R. L. De, *J. Mol. Catal. A: Chem.* 2007, **265**, 244.
28 V. Polshettiwar, R. S. Varma, *Tetrahedron Lett.* 2007, **48**, 8735.
29 B. Das, N. Chowdhury, *J. Mol. Catal. A: Chem*. 2007, **263**, 212.
30 K. R. Reddy, N. S. Kumar, *Synlett,* 2006, **14**, 2246.
31 G. Bartoli, M. Bartolacci, A. Giuliani, E. Marcantoni, M. Massaccesi, E. Torregiani, *J. Org. Chem.* 2005, **70**, 169.
32 L. Dai, Y. Zhang, Q. Dou, X. Wang, Y. Chen, *Tetrahedron*, 69 2013, **69**, 1712.
33 L. N. Monsalve, F. Gillanders, A. Baldessari, *Eur. J. Org. Chem.* 2012, **6**, 1164.
34 K. P. Dhake, P. J. Tambade, R. S. Singhal, B. M. Bhanage, *Tetrahedron Lett.* 2010, **51**, 4455.
35 J. Christoffers, *Eur. J. Org. Chem*. 1998, 1259.
36 J. Clariana, N. Galvez, C. Marchi, M. M. Manas, A. Vallribera, E. Molins, *Tetrahedron,* 1999, **55**, 7331.
37 N. Giuseppone, Vander P. Weghe, M. Mellah, J. Collin, *Tetrahedron,* 1998, **54**, 13129.
38 A J. Bolton, *Mat. Tech.* 1994, **9**, 12.
39 E. Guibal, *Progr. Polym. Sci.* 2005, **30**, 71.
40 D. W. O'Connell, C. Birkinshaw, T. F. O'Dwyer *A Review. Bioresources Technololgy*, 2008, **99**: 6709.
41 W. Dahou, D. Ghemati, A. Oudia, D. Aliouche, *Biochem. Engi. J.* 2010, **48**, 187.
42 W. L. Wei, H. Y. Zhu, C. L. Zhao, M. Y. Huang, Y.-Y. Jiang, *React. Funct. Polym.* 2004, **59**, 33.
43 X. Zhang, Y. Geng, B. Han, M. Y. Ying, M. Y. Huang, Y. Y. Jiang, *Polym. Adv. Technol.* 2001, **12**, 642.
44 K. Huang, L. Xue, Y. C. Hu, M. Y. Huang, Y.-Y. Jiang, *React. Funct. Polym.* 2002, **50**, 199.
45 F. Quignard, A. Choplin, A. Domard, *Langmuir,* 2000, **16**, 9106.
46 M. L. Rahman, N. R. N. Mustapa, M. M. Yusoff*, J. Appl. Polym. Sci*. 2014, **131**, 40833.
47 M. L. Rahman, S. Silong, W. M. Z. W. Yunus, M. Z. A. Rahman, M. Ahmad, J. Haron, *Euro. Polym. J.* 2000, **36***,* 2105.
48 W. S. S. Yong, M. L. Rahman, S. E. Arshad, N. L. Surugau, B. Musta, *J. Appl. Polym. Sci.* 2012**, 124***,* 4443.
49 M. L. Rahman, S. Silong, W. M. Z. W. Yunus, M. Z. A. Rahman, M. Ahmad, J. Haron, *J. App. Polym. Sci*. 2001**, 79***,* 1256.
50 F. L. Chuan, L. R. Jun, X. Feng, J. L. Jina, X. S. Jin, C. S. Run, *J. Agric. Food. Chem*. 2006**, 54**, 5742.
51 E. Prenesti, S. Berto, *J. Inorg. Biochem.* 2002*,* **88**, 37.
52 Z. Huang, F. Li, B. Chen, F. Xue, G. Chen, G. Yuan, *Appl. Catal. A. Gen.* 2011, **403**, 104.

Graphical abstract

Waste corn-cob cellulose supported Cu-nanoparticle was found as a highly effective catalyst for Aza-Michael reaction at room temperature.



R^1, R^2 = alkyl

up to 96% yield
1st run: 96%; 8th run: 91%