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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C6RA00102E

Copper(II) supported on magnetic chitosan: A green nanocatalyst for the synthesis of 2,4,6-triaryl pyridines by C-N bond cleavage of benzylamines

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Abstract

In this paper, Cu/magnetic chitosan has been synthesized and used as a new green nanocatalyst for a highly efficient synthesis of 2,4,6-triaryl pyridines *via* a C-N bond cleavage of benzylamines under aerobic oxidations at 90 °C. The chemical and structural properties of the synthesized catalyst were determined by scanning electron microscopy, energy-dispersive X-ray, X-ray powder diffraction, thermogravimetric analysis and flame atomic absorption spectroscopies. It is found that the catalyst can be easily separated from the reaction mixture by an external magnetic field and be recycled for several times without a significant loss of activity.

Keywords:

Chitosan, heterogeneous catalyst, copper, magnetic, triarylpyridines, C-N bond cleavage

1. Introduction

In recent years, developing routs to produce materials based on green chemistry which minimizes pollution have been focused.[1] To reach these goals, the development of heterogeneous catalysts in the synthesis of organic compounds is highly investigated due to the ease of handling, reusability and simple work-up.[2] Immobilization of precious-metal and nonprecious-

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metal catalysts on various inorganic, petrochemical derived polymers and other synthetic polymers to produce heterogeneous catalytic systems has been widely reported.[3-9] Nevertheless the enthusiasm for a cleaner and sustainable chemistry has resulted in exploiting abundant natural polymers such as chitosan (Cs) for catalytic applications due to its high surface area, low cost, biocompatibility, biodegradability, and non-toxicity.[10-12]

Chitin is the second most abundant natural polymer after cellulose which can be found in insects, fungi, shrimps and crabs.[13] Chitosan (Cs), a chemically stable, non-toxic and biodegradable polysaccharide prepared from chitin, is an excellent candidate to be used as a support for copper,[14-17] ruthenium,[18] rhodium,[19] cerium[20] and other transition metals due to its insolubility in organic solvents and the presence of functionalizable amino groups in the structure. In addition, mesoporous, nitrogen-containing carbon materials obtained directly from pure chitin are used as an absorbent to remove toxic heavy metals and as a catalyst for epoxidation of styrene.[21] Although chitin and chitosan have been used in industrial chemistry such as textile, cosmetics and biomedicine, they also have a significant potential for a sustainable production of small nitrogen-containing chemicals such as ethanolamine.[22] Nowadays, various investigations have been carried out to develop new protocols for an efficient conversion of chitin to value–added chemicals.[23-26]

In recent decade, the synthesis of supported magnetic nanoparticles has attracted a considerable attention in catalyst science due to their availability, low toxicity, high catalytic activity, excellent surface area and magnetic separability thereby eliminating the filtration process after the end of reactions.[27] Immobilization of iron oxide nanoparticles on biodegradable polymers such as cellulose and chitosan has produced highly efficient adsorbents for the removal of metals, drug carriers and reusable nano catalysts.[28-32] To the best of our knowledge, there is no

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report in which copper(II) magnetic chitosan nanocomposite has been used for an organic transformation.

The C-N bond cleavage is an important synthetic strategy that has been widely investigated.[33] It is known that transition metals, such as palladium,[34] ruthenium,[35] and copper[36] are catalysts which promote the C-N bond cleavage and the C-N bond formation. Specially, the application of copper-based catalysts in this reaction is remained as a considerable topic due to the low toxicity and cost of copper compared to other more common noble metals. Recently Wang et al. reported the C−N bond cleavage and the formation for the synthesis of benzimidazo[1,2-a]quinazoline derivatives using CuI/L-proline.[37] Jiang et al. developed an efficient copper-catalyzed C−N bond cleavage of aromatic methylamines to construct pyridine derivatives,[38].

Pyridine rings are one of the most important heterocyclic moieties which have many applications in natural products, organic and medical chemistry and functional materials.[39] Pyridines synthesis is an interesting topic in modern synthetic chemistry among which, 2,4,6-trisubstituted pyridine derivatives have been used in supramolecular chemistry due to their p-stacking ability along with H-bonding capacity.[40] The development of new heterogeneous catalysts for the synthesis of multi-substituted pyridines is in high demand.[41-42]

In continuation of our interest in the sustainable benign pathway for organic transformations and nanocatalysis,[43-48] we wish to introduce the synthesis of 2,4,6-triaryl pyridine derivatives by the C-N bond cleavage of benzyl amines in the presence of Cu (II) immobilized on magnetic chitosan as a nanocatalyst. The obtained catalytic system, Cu/magnetic chitosan, exhibits a high activity and selectivity for the synthesis of 2,4,6-triaryl pyridine derivatives under aerobic conditions. The catalyst can be separated from the reaction mixture

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using an external magnetic field and be reused for five consecutive reaction times without a significant decrease in the catalytic activity.

2. Experimental

2.1.Materials and Methods

Chitosan (molecular weight: 100,000-300,000) was purchased from Acros Organics. Iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, copper(II) chloride dehydrate and sodium hydroxide were purchased from Sigma Aldrich. Dimethylsulfoxide (DMSO), dimethylformamide (DMF), toluene, acetophenone, 4′-methylacetophenone, 4′-chloroacetophenone, 4′-bromoacetophenone, benzylamine, 4-methylbenzylamine, 4-chlorobenzylamine, 4-methoxybenzylamine, and 2-picolylamine were purchased from Sigma Aldrich. All chemicals were used without further purifications.

The FT-IR spectra were recorded on a Bomem MB-Series FT-IR spectrometer. The thermal analysis (TGA-DTA) was carried out using a Bahr STA-503 instrument at a heating rate of 10 °C min^{-1} in air. The X-ray powder diffraction (XRD) pattern was recorded on a STOE diffractometer with Cu-K_α radiation (λ= 015418 nm). The scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDS) characterization of catalyst were performed using an electron microscopy Philips XL-30 ESEM. All the samples were sputtered with gold before observation. The ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer. The NMR spectra were obtained in $CDCl_3$ and DMSO-d_6 using the tetramethyl silane (TMS) as internal standard. The melting points of the products were measured by an electrothermal 9100 apparatus. The concentrations of copper and iron were estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and an inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The XPS analysis

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was performed using a Gammadata-scientifica ESCA 200 hemispherical analyzer equipped with an Al Kα (1486.6 eV) X-ray source.

2.2.General procedure for synthesis of magnetic chitosan nanoparticles (MCs)

The synthesis of Fe_3O_4 nanoparticles with Cs was carried out according to the literature which has described procedures.[32] An aqua solution of $FeCl_3 \cdot 6H_2O$ (27.0 mg) and $FeCl_2 \cdot 4H_2O$ (9.95 mg) with a molar ratio of 2:1 in 5 mL distilled water was prepared and added to a suspension of the Cs (30.0 mg) in 20 mL distilled water under a vigorous stirring under nitrogen atmosphere. After stirring for 10 min, the sodium hydroxide solution was added to the mixture and the stirring was strongly continued for 4 h at 80 ºC. After cooling the suspension to the room temperature, the MCs was separated by the magnet decantation, was washed with distilled water, ethanol and, finally was dried under the vacuum at the room temperature.

2.3.General procedure for synthesis of MCs-Cu(II) nanocatalyst

The MCs (0.1 g) was suspended in 20 mL of distilled water and 0.03 g of $CuCl_2.2H_2O$ was added to the mixture and stirring was continued for 3h. The catalyst was separated using a magnet and was dried under the vacuum at 50 °C.

2.4.General procedure for synthesis of copper nanoparticles@magnetic chitosan

The copper nanoparticles@magnetic chitosan was synthesized according to the pervious report.[49] Briefly, 0.5 g of the magnetic chitosan was dispersed in 25 ml of ethanol in a 100 ml round-bottomed flask, after which 25 ml (0.25 mmol) of the ethanolic solution of the copper(II) acetate was added dropwise under vigorous stirring. After 4h of stirring, the copper ions were completely adsorbed by chitosan and the MCs-$Cu(CH_3COO)_2$ was separated by an external magnet and was dried in a desiccator. The dried MCs-$Cu(CH_3COO)_2$ was again dispersed in 50

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ml of methanol and 15 ml of $NaBH_4$ (5 mmol) solution was added slowly under vigorous string under nitrogen atmosphere. The copper nanoparticles@magnetic chitosan were separated by an external magnet and washed several times with methanol and then dried in the desiccator.

2.5.General procedure for preparation of 2,4,6-triaryl pyridines

A ketone (2 mmol), benzylamine (1.2 mmol), MCs-Cu (II) nanocatalyst (0.064 g, 5 mol %) were added to a 25 mL tube. The mixture was stirred for 8 h at 90 °C. Upon completion; acetone was added to the mixture and the catalyst was separated by an external magnet. The solid product was recrystallized from acetone-water 9:1 (v/v) to produce the pure product.

2.6.Product characterization data of 2,4,6-triaryl pyridines

2,4,6-Triphenylpyridine (3a), yield: 90, $C_{23}H_{17}N$, white solid, FT-IR (KBr) cm^{-1}: 1450-1600, 758, 692 ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.23 (d, J= 7.5 Hz, 4H), 7.9 (s, 2H), 7.7 (d, J= 6.9, 2H), 7.2-7.9 (9H, m, H-Ar), ^{13}C NMR (75.47 MHz, $CDCl_3$): 117.02, 127.40, 128.72, 129.68, 129.73, 139.19, 139.26, 150.06, 157.02.

2,6-Diphenyl-4-(*p*-tolyl)pyridine (3b), yield:91, $C_{24}H_{19}N$, white solid, FT-IR (KBr) cm^{-1}: 3020, 2950, 1450-1600, 759, 692. ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.2 (d, 4H), 7.9 (s, 2H), 7.7 (d, 2H), 7.2-7.9 (9H, m, H-Ar), ^{13}C NMR (75.47 MHz, $CDCl_3$): 21.25, 116.66, 127.54, 129.17, 129.63, 130.14, 135.18, 139.41, 156.96.

4-Phenyl-2,6-di-*p*-tolylpyridine (3c), yield: 90, $C_{25}H_{21}N$, white solid, FT-IR (KBr) cm^{-1}: 3022, 2950, 1450, 1600, 757, 695. ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.13 (d, J= 7.8 Hz, 4H), 7.87 (s, 2H), 7.76 (d, J=7.2 Hz, 2H), 7.47-7.58 (m, 3H), 7.34 (d, J=7.8 Hz, 4H), 2.46 (s,6 Hz), ^{13}C NMR (75.47 MHz, $CDCl_3$): 21.30, 116.42, 126.90, 127.12, 128.82, 129.10, 129.35, 136.80, 138.92, 139.20, 149.93, 157.32

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2,4,6-Tri-*p*-tolylpyridine (3d), yield: 92, $C_{26}H_{23}N$, white solid, FT-IR (KBr) cm^{-1}: 3022, 2950, 1450, 1600, 757, 695. ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.12 (d, J= 7.8 Hz, 4H), 7.86 (s, 2H), 7.78 (d, J=7.8 Hz, 2H), 7.33-7.36 (m, 3H), 2.46 (s,9 Hz), ^{13}C NMR (75.47 MHz, $CDCl_3$): *δ* 21.35, 21.43, 116.44, 127.07, 127.12, 129.48, 129.87, 136.20, 136.83, 139.04, 139.07, 150.03, 150.326

2',6'-Diphenyl-2,4'-bipyridine (3e), yield: 95, $C_{22}H_{16}N_2$, yellow solid, FT-IR (KBr) cm^{-1}: 3059, 1594, 1488, 1321, 830, 770, 690. ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.18-8.28 (m, 6H), 7.85-7.93 (m, 2H), 7.76 (t, J=7.5 Hz, 2H), 7.47-7.59 (m,6 Hz), ^{13}C NMR (75.47 MHz, $CDCl_3$): *δ* 119.13, 126.43, 127.20, 127.52, 127.70, 128.92, 129.49, 129.54, 129.87, 137.09, 139.40, 148.01, 157.33.

2,6-*Bis*(4-chlorophenyl)-4-phenylpyridine (3f), yield: 90, $C_{23}H_{15}Cl_2N$, white solid, FT-IR (KBr) cm^{-1}: 3052, 1489, 1486, 1597, 1524, 760, 694, ^1H NMR (300.13 MHz, DMSO-d_6), δ 8.36 (d, J= 8.4 Hz, 4H), 8.23 (s, 2H), 8.04 (d, J=7.6 Hz, 2H), 7.50- 7.61 (m, 7H), ^{13}C NMR (75.47 MHz, DMSO-d_6): δ, 117.31, 127.87, 129.20, 129.55, 129.71, 129.91, 134.65, 137.86, 150.31, 155.75.

4-(4-Chlorophenyl)-2,6-diphenylpyridine (3g), yield: 95, $C_{23}H_{16}ClN$, white solid, FT-IR (KBr) cm^{-1}: 3061, 1599, 1545, 1489, 775, 692, ^1H NMR (300.13 MHz, DMSO-d_6), δ 8.12 (d, J=7.2 Hz, 4H), 8.14 (s, 2H), 7.91 (d, J=8 Hz, 2H), 7.41 (d, J=6.8 Hz, 2H), 7.28-7.36 (m, 6H), ^{13}C NMR (75.47 MHz, DMSO-*d6*): δ, 116.88, 127.44, 129.17, 129.47, 129.64, 134.70, 136.94, 139.18, 148.64, 157.05.

4-(4-Methoxyphenyl)-2,6-diphenylpyridine (3h), yield: 85, $C_{24}H_{19}NO$, white solid, FT-IR (KBr) cm^{-1}: 3035, 1596, 1547, 1486, 750, 690, ^1H NMR (300.13 MHz, $CDCl_3$), δ 8.30 (d, J=7.2 Hz,

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4H), 8.15 (s, 2H), 7.93 (d, J=8 Hz, 2H), 7.45-7.55 (m, 6H), 7.34-7.36 (d, J=8 Hz, 2H), 3.36 (s,3H), (^{13}C NMR 75.47 MHz, $CDCl_3$): δ, 55.80, 114.80, 118, 127.60, 128.40, 129.30, 130.20, 152, 155.20, 161.10.

3. Results and discussion

The magnetic chitosan nanoparticles were prepared by the chemical co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio 2:1.[32] Then, the immobilization of copper on the magnetic chitosan was carried out in an aqueous solution of copper (II) chloride for 3 h under neutral conditions.[17]

Figure 1 shows the XRD patterns of the chitosan and the MCs-Cu (II) nanocatalyst. There are six characteristic peaks at 2θ= 30.04 °, 35.5°, 43.12°, 53.44°, 57.04° and 62.8° in the XRD pattern of the MCs-Cu (II) nanocatalyst that confirm the standard pattern with a spinel structure for the crystalline magnetite (JCPDS card no. 01-1111). Because of the diffraction peaks of Fe_3O_4 are stronger than the diffraction peaks of chitosan, the peaks related to the chitosan were not observed.[32] According to the Scherrer's equation the mean crystallite size calculated was 23 nm.

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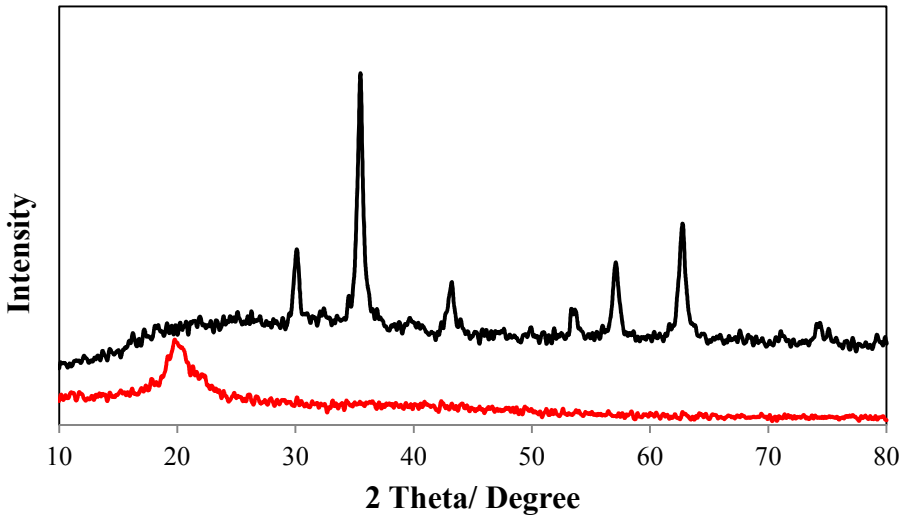

Figure 1. The XRD patterns of chitosan (red) and the MCs-Cu (II) nanocatalyst (black)

The Cu (II) loading on the MCs-Cu(II) nanocatalyst was determined as 5 wt % based on the FAAS analysis. The Fe loading level of catalyst was measured by ICP-AES and it was obtained 16.67 wt %.

Thermogravimetric analysis (TGA) was used in order to obtain information on the thermal stability of the chitosan and the MCs-Cu (II) nanocatalyst (Figure 2). The TGA results confirm that the Cs was stable over 200 °C and there were three steps of mass losses for the catalyst in the temperature range of 50-260 °C, 260-315 °C and 315-520 °C. The weight loss of the catalyst is about 74 % that corresponding to the thermal decomposition of the chitosan.

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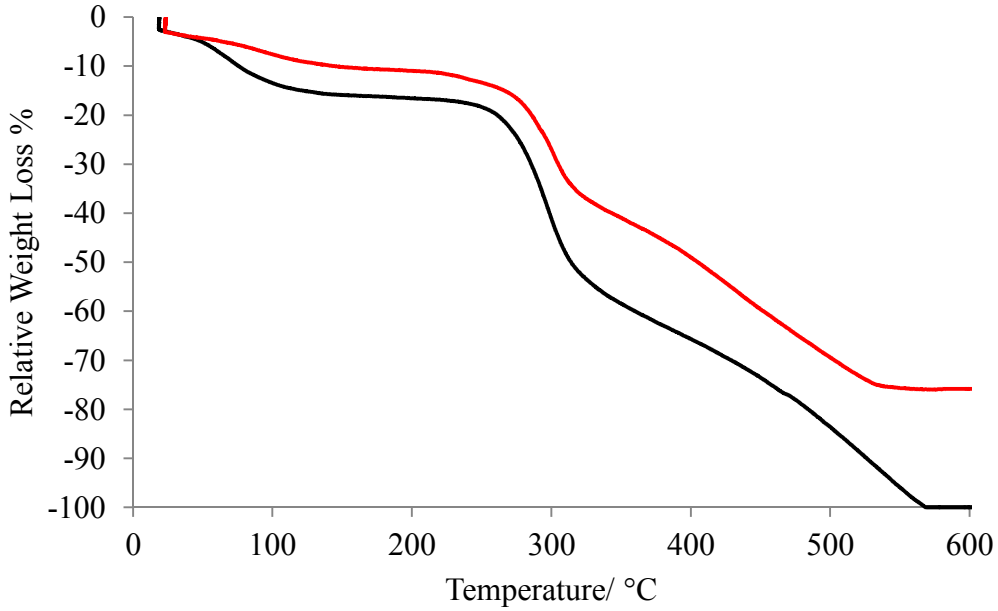

Figure 2. The TGA thermogram of the chitosan (black) and the MCs-Cu(II) nanocatalyst (red)

The SEM analysis was used to study the morphology and the structure of the MCs-Cu (II) nanocatalyst. The SEM images show an excellent dispersity of Fe_3O_4 nanoparticles on the Cs (Figure 3). Also, the energy dispersive spectroscopy (EDS) analysis clearly illustrates the presence of iron and copper in the nanocatalyst (Figure 4).

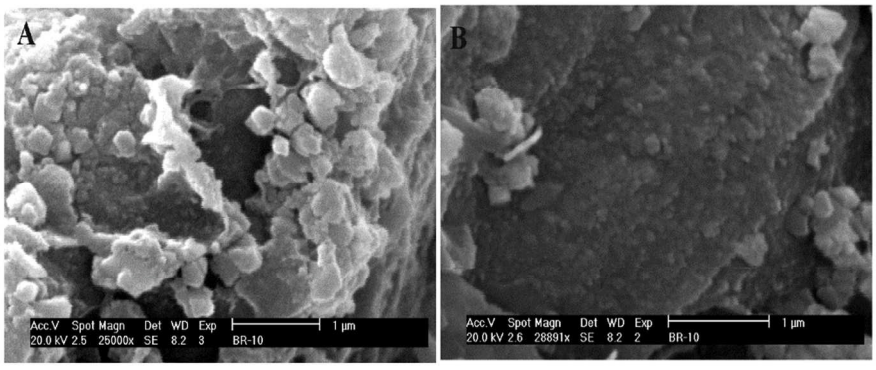

Figure 3. The SEM image of the MCs-Cu(II) nanocatalyst (A,B)

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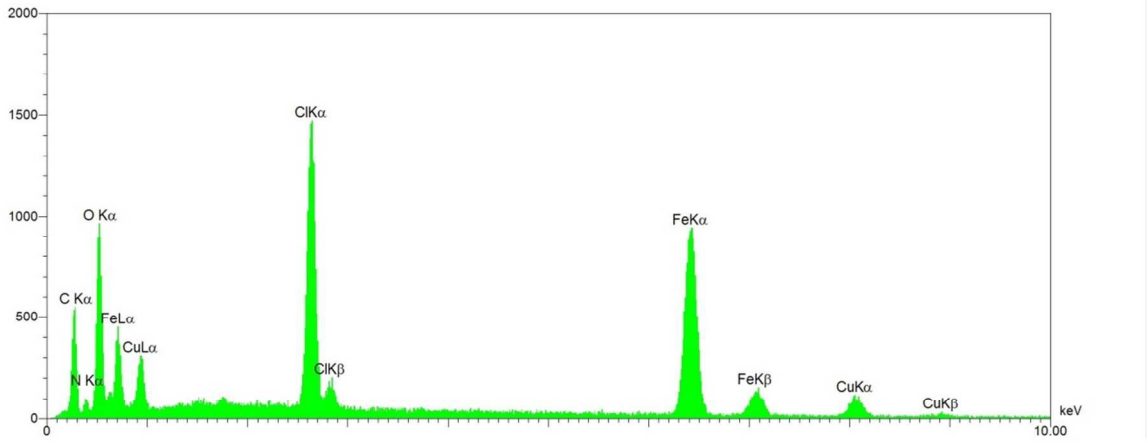

Figure 4. The (EDS) analysis of The MCs-Cu(II) nanocatalyst

To show the efficiency of the MCs-Cu(II) as a nanocatalyst, we investigated the reaction of acetophenone (2 mmol) and benzylamine (1.2 mmol) for the synthesis of 2,4,6-triaryl pyridine derivates in toluene for 12 h under aerobic oxidation in the presence of various amounts of the catalyst (Table 1). The reaction in the absence of the catalyst did not result in the foremetioned product (Table1, Entry 1). In addition, in the presence of the magnetic chitosan, no reaction occurred even after 8 h (Table1, Entry 2). As the amount of the catalyst was increased (5 mol%), the reaction went to completion at 90 °C (Table1, Entries 3-6) . This reaction in the presence of $CuCl_2$ as a homogeneous catalyst in the air gave the 2,4,6-triaryl pyridines in 40% yield (Table 1, Entry 7). However, the separation of the catalyst from the reaction mixture was difficult. The yield of reaction in oxygen atmosphere was not increased (Table1, Entry 8).

For more investigation, copper nanoparticles@magnetic chitosan were prepared [49] and used for this reaction. As shown in Table 1, the yield of the reaction in the presence of the copper nanoparticles@magnetic-chitosan was not significantly changed compared to that in the presence of the MCs-Cu(II) nanocatalyst. Therefore, the MCs-Cu(II) nanocatalyst was found to be a better catalyst than the copper nanoparticles@magnetic chitosan due to its simple preparation. (Table 1,

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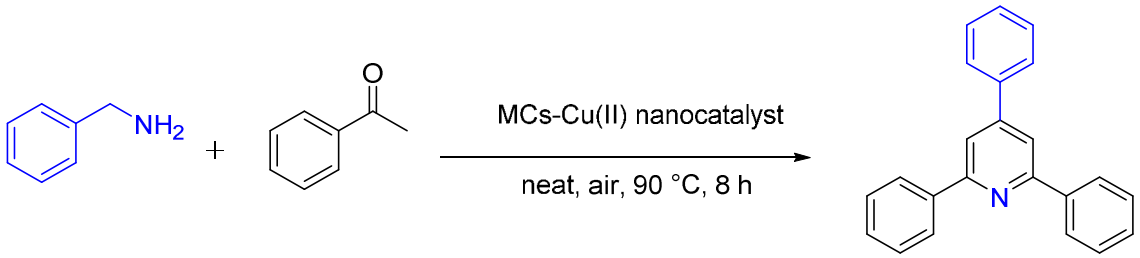
Entry 9). Next, various solvents were used to study their effect on the yield of product. Surprisingly, the reaction did not show a strong solvent dependence. Also, using toluene had no efficient influence on the transformation (Table1, Entry 10-14). Thus, the reaction was carried out under solvent free conditions. After screening different temperatures, 90 °C was obtained as the best temperature for the reaction. The optimized conditions for the synthesis of the 2,4,6-triaryl pyridines were 5 mol% of the catalyst in the absence of any additive or solvent under the air at 90 °C.

Table 1. Screening the reaction conditions [a]



Entry	Catalyst (mol%)	Solvent	Oxidant	Temperature (°C)	Yield [b] (%)
1	None	toluene	air	90	0
2	MCs	toluene	air	90	0
3	MCs-Cu(II) nanocatalyst (1)	toluene	air	90	30
4	MCs-Cu(II) nanocatalyst (3)	toluene	air	90	60
5	MCs-Cu(II) nanocatalyst (5)	toluene	air	90	90
6	MCs-Cu(II) nanocatalyst (8)	toluene	air	90	90
7	$CuCl_2$ (5)	toluene	air	90	40
8	MCs-Cu(II) nanocatalyst (5)	toluene	O_2	90	90
9	Copper nanoparticles@magnetic-Chitosan (5)	toluene	air	90	90
10	**MCs-Cu(II) nanocatalyst (5)**	**neat**	**air**	**90**	**90**

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11	MCs-Cu(II) nanocatalyst (5)	toluene	air	90	88
12	MCs-Cu(II) nanocatalyst (5)	water	air	90	60
13	MCs-Cu(II) nanocatalyst (5)	DMSO	air	90	70
14	MCs-Cu(II) nanocatalyst (5)	DMF	air	90	40
15	MCs-Cu(II) nanocatalyst (5)	neat	air	70	60
16	MCs-Cu(II) nanocatalyst (5)	neat	air	110	90

[a] Reaction conditions: acetophenone (2.00 mmol), benzylamine (1.2 mmol), catalyst, air (1 atm), 8 h.

[b] isolated yield

With the optimized reaction conditions established, the scope of benzylamines and methyl ketones was examined to explore the generality of the 2,4,6-triaryl pyridines synthesis under the aerobic conditions.

Acetophenones derivatives with a wide array of functional groups such as chloro, bromo and methyl on the aryl group were employed to synthesis of the 2,4,6-triaryl pyridines. Phenyl methyl ketones with electron-withdrawing or electron-donating substituents on the aromatic ring result in the forementioned product. Using nonmethyl ketones such as cyclohexanone did not led to the desired product. Substituted benzyl amines were employed to give the desired pyridines in good yields. According to theprevious report,[38] under the homogeneous copper-catalysed system, 2-pyridylmethylamine with methyl ketone could not produce the 2,4,6-triaryl pyridines.[38] However, in the case of our reaction conditions, using the MCs-Cu(II) nanocatalyst, the 2,4,6-triaryl pyridines were produced from the reaction of 2-pyridyl methylamines with methyl ketones (Table 2, Entry 5).

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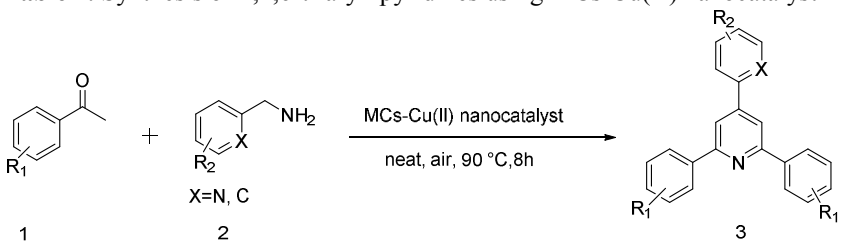
Table 2. Synthesis of 2,4,6-triaryl pyridines using MCs-Cu(II) nanocatalyst [a]



1 2 3

Entry	R_1	R_2	Product	Yield % [b]	Melting point
1	H	H	3a	90	135-138
2	H	CH_3	3b	85	118-120
3	CH_3	H	3c	85	154 - 156 °C
4	CH_3	CH_3	3d	80	174 - 176 °C
5	H	H, X=N	3e	90	98-100 °C
6	Cl	H	3f	80	175 - 178
7	H	Cl	3g	85	127-128
8	H	OMe	3h	80	99-101
9	Cl	OMe	3i	75	190-192
10	Br	H	3j	70	98-100

[a] Reaction conditions: 1(2 mmol), 2 (1.2 mmol), MCs-Cu(II) nanocatalyst (0.064 g, 5 mol %), air, at 90 °C for 8 h. [b] isolated yield

It is important to note that the cross reactions with two different methyl ketones provided asymmetric 2,4,6-triaryl pyridines as a major product. For example, when benzylamine (1.2 mmol) and *p*-methylacetophenone (1 mmol) were treated with acetophenone (1 mmol), the 2,4,6-triaryl pyridines were synthesized in a moderate yield. The results are summarized in Table 3.

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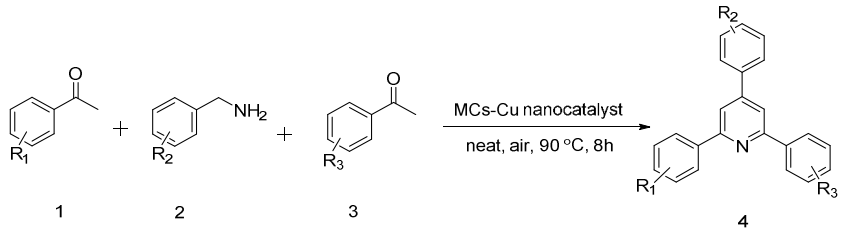
Table 3. The Synthesis of the asymmetric 2,4,6-triaryl pyridines using the MCs-Cu(II) as a nanocatalyst [a]



1 2 3 4

Entry	R_1	R_2	R_3	product	Melting point	Yield % [b]
1	H	H	CH_3	4a	123 - 124	60
2	H	CH_3	CH_3	4b	133-135	50

[a] Reaction conditions: 1(1 mmol), 2 (1.2 mmol), 3 (1 mmol), MCs-Cu(II) nanocatalyst (0.064 g, 5 mol %), air, at 90 °C for 8 h. [b] isolated yield

Based on the previous reports, [38,50-58] a plausible mechanism was proposed in Scheme 1. At first, single-electron transfer oxidation of benzylamine occurred in the presence of the MCs-Cu(II) nanocatalyst and then imine was produced from the aminolysis reaction. Next the hydrolysis of imine as a reversible process could provide benzylamine and benzaldehyde. The condensation of benzaldehyde, ketone, and benzylamine in the presence Cu(II) as a Lewis acid produced 1,4-dihydropyridine intermediate. Finally, the 2,4,6-triaryl pyridine was produced from the oxidation of 1,4 dihydropyridine intermediate under the catalytic aerobic conditions.

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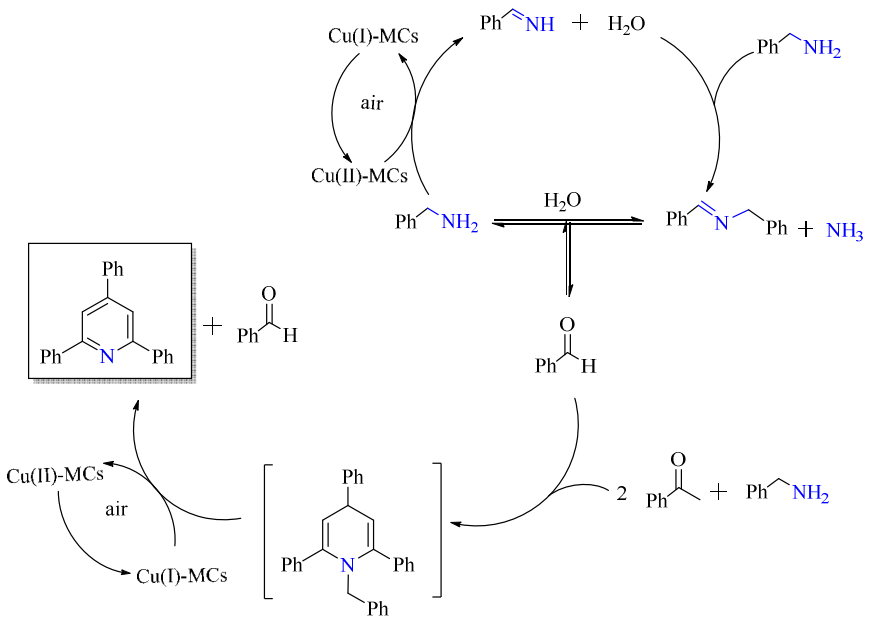

Scheme 1. Plausible reaction mechanism

The stability of the MCs-Cu(II) nanocatalyst toward the leaching of copper ions was examined, as well. Briefly, a mixture of ketone and benzylamine in the presence of catalyst was stirred in toluene at 90 °C for 15 min, next the catalyst was separated by an external magnet from the reaction mixture and the reaction was continued by catalyst-free mixture under the same conditions for an additional 8 h. the yield of the reaction was 10 % before the filtration of the catalyst and the final yield was 11%. Also, according to the FAAS analysis results, the leaching of the copper ions in to a solution phase was less than 0.5% . This means that the leaching of copper should be negligible.

The recyclability of the MCs-Cu(II) nanocatalyst was surveyed for the synthesis of the 2,4,6-triaryl pyridines under the optimized conditions at 90 °C. After the reaction time, the solid catalyst was separated by an external magnet, was washed and dried at 80 °C and was used in the next run without further treatment. It was observed that in the next five consecutive uses of the

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MCs-Cu(II) nanocatalyst, the catalytic activity and selectivity did not significantly decrease (Figure 5).

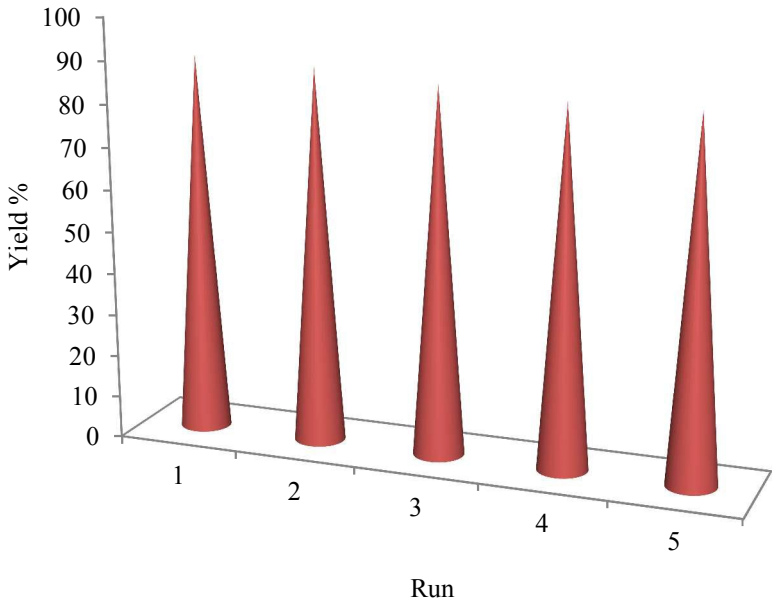

Figure 5. Recycle of the MCs-Cu(II) nanocatalyst for the synthesis of 2,4,6-triaryl pyridines

The XPS analysis of the catalyst after five runs of the reaction was shown in Figure 6. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ were clearly observed at 934.05 and 954.12 eV, respectively, that confirm the Cu(II) ions in the catalyst were stable under the reaction conditions.[59]

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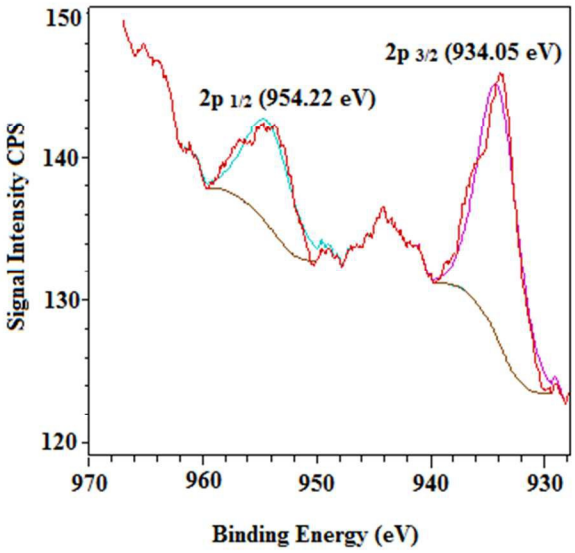

Figure 6. The cu 2p core-level XPS spectrum of the MCs-Cu(II) nanocatalyst

4. Conclusion

The MCs-Cu(II) nanocatalyst was synthesized by a uniform distribution of Fe_3O_4 nanoparticles on the chitosan matrix. The new catalyst successfully promoted the synthesis of the 2,4,6-triaryl pyridines *via* a C-N bond cleavage of benzylamine under aerobic oxidations with fairly good yields. The reaction was carried out under environmentally benign, solvent-free and aerobic conditions. The structure of the catalyst was confirmed by the XRD, TGA, EDS and the SEM. The MCs-Cu(II) nanocatalyst showed advantages such as magnetic separablitiy, recyclability, good chemical stability, low solubility in organic solvents, and a uniform distribution of the nanoparticles on the chitosan. The leaching tests indicated that the reaction was mainly heterogeneous in nature.

Acknowledgments

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DOI: 10.1039/C6RA00102E

We gratefully acknowledge financial support from the Catalyst Center of Excellence (CCE) of Shahid Beheshti University and the Iran National Elites Foundation (INEF).

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DOI: 10.1039/C6RA00102E

Copper(II) supported on magnetic chitosan: A green nanocatalyst for the synthesis of 2,4,6-triaryl pyridines by C-N bond cleavage of benzylamines

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