



Inorganic and Nano-Metal Chemistry

ISSN: 2470-1556 (Print) 2470-1564 (Online) Journal homepage: https://www.tandfonline.com/loi/lsrt21

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To cite this article: Saeed Zahmatkesh, Mohsen Esmaeilpour & Azade Mollaiy Poli (2019): Ligand complex of copper (II) supported on superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles: an efficient and magnetically separable catalyst for N-arylation of nitrogen-containing heterocycles with aryl halides, Inorganic and Nano-Metal Chemistry, DOI: 10.1080/24701556.2019.1618326

To link to this article: https://doi.org/10.1080/24701556.2019.1618326



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Ligand complex of copper (II) supported on superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles: an efficient and magnetically separable catalyst for *N*-arylation of nitrogen-containing heterocycles with aryl halides

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ABSTRACT

In this study, we introduce the ligand complex of copper (II) supported on superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles as a highly intriguing magnetic catalyst in *N*-arylation of nitrogen heterocycles with aryl halides. The present methodology offers several advantages such as; low catalyst loading, the use of magnetically recoverable and reusable catalyst, high to excellent yields without using any external ligands or additives, short reaction times and simplicity of operation. Also, the magnetic catalyst could be easily separated from the final product by an external magnet and reused up to seven times without any significant loss of activity. Therefore, this separation strategy with negligible leaching makes $Fe_3O_4@SiO_2/ligand/Cu(II)$ an economical catalyst to perform this transformation.

ARTICLE HISTORY

Received 30 April 2017 Accepted 21 November 2018

KEYWORDS

Magnetic heterogeneous nanoparticles; core-shell; *N*-Arylation; nitrogen heterocycles; aryl halides; copper; magnetic separation

1. Introduction

Magnetic nanoparticles have attracted much interest in recent years due to its unique magnetic properties, feasibility of preparation, low toxicity, high specific surface area, their unique catalytic and their wide applications, including magnetically targeted drug and gene delivery, magnetic bioseparation, enzyme immobilization, magnetic resonance imaging (MRI) contrast agents, magnetic mediated hyperthermia for cancer treatment, ion exchange separation, magnetic data storage, biosensors and environmental remediation and catalysis.^[1-6] However, the magnetic Fe₃O₄ nanoparticles trend to aggregate due to their nanoscale and strong interaction between each other.^[7, 8] In addition, since magnetite NPs contain Fe²⁺, which is easily oxidized, they are vulnerable to a loss in magnetism.^[9] Therefore, a protection laver is required to ensure Fe₃O₄ nanoparticles chemical stability and improve their dispersibility. Various inorganic and polymeric materials have been reported as carriers of magnetic materials.^[10-12] Among them, mesoporous silica possesses numerous favorable properties, including large pore volume, low cytotoxicity, tunable pore size, high surface area, and excellent biocompatibility.^[13–15] In addition, its silanol surfaces are easily modified with a variety of functional groups. Magnetic nanoparticles embedded in a silica matrix can screen the magnetic dipolar interactions between magnetic nanoparticles, which protect magnetic nanoparticles from leaching in an acidic environment and favor the dispersion of them in liquid media.^[16-18] Therefore, in recent years, considerable attentions have been paid to the preparation and application of silica-coated magnetite ($Fe_3O_4@SiO_2$) because of their unique magnetic response, low cytotoxicity, and chemically modifiable surface.^[19–22]

The formation of carbon-nitrogen bonds via cross-coupling reactions has attracted a great deal of interest recently due to their importance in fields such as natural products, photograph and materials.^[23-25] For this reason, transitionmetal-catalyzed arylation of nitrogen containing heterocycles with aryl halides is one of the most efficient and powerful methods for the N-arylation reactions and has proven useful in both academic and industrial laboratories. In these reactions a variety of different metal catalysts such as Ni, Cu, and Pd are employed alone or with different coordinating ligands such as phosphor amides, oxime-phosphine oxides, ethylene glycol, bisamines, Schiff bases, diethyl salicylamide, DPPF, and amino acids.^[26-32] These ligands play an important role in controlling the concentration of active catalytic species, but they may contaminate the final product. Thus, using a catalyst in the absence of any additional ligands could be a good alternative to avoid the inconvenience of ligand removal from the reaction mixture. On the other hand, due to the economic attractiveness and vast abundance of copper, many Cu-catalyzed C-N bond formation reactions have led to a resurgence of interest in carbon-heteroatom coupling reactions, and their applications seem to be of more and more importance.^[33, 34] Therefore, the copper-mediated Ullmann coupling reaction is still the

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straightforward method to form the requisite carbon-heteroatom bonds. There have been numerous copper mediated or copper-catalyzed methods published to allow for such a transformation.^[37-39] However, these reports, while significant contributions, generally suffer from important limitations such as high reaction temperatures, stoichiometric amount of copper reagents, poor substrate generality and many functional groups could not be tolerated. Therefore, development of new methodology taking into consideration a decrease of reaction time, minimum metal contamination of products, a simple catalyst system involving easy isolation and reusability of catalysts, and ligand-free conditions is highly desirable.

Accordingly, in continuation of our studies on the synthesis of novel supported catalysts,^[40, 41] herein we report a simple and efficient method for *N*-arylation of nitrogen heterocycles with aryl halides in the presence of ligand complex of copper (II) supported on superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles as illustrated in Scheme 1.

2. Results and discussions

In previous work,^[42] we report a new method for preparing ligand complex of copper (II) supported on superparamagnetic Fe₃O₄@SiO₂ nanoparticles. Magnetite particles were prepared by simple co-precipitation method in aqueous medium, and then Fe₃O₄@SiO₂ nanoparticle was synthesized by using nano magnetite as the core, TEOS as the silica source and polystyrene (PS 35000) as the surfactant. Then, ligand complex of copper (II) was supported on Fe₃O₄@SiO₂/Ligand/Cu(Π) nanocatalyst was characterized by FT-IR, FE-SEM, TEM, DLS, TGA, VSM, EDS and ICP methods.^[42] Scheme 2 presents the procedure for the preparation of Fe₃O₄@SiO₂/Ligand/Cu(Π) stepwise.

Figure 1 shows the FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂, Fe₃O₄@SiO₂/ligand and Fe₃O₄@SiO₂/ligand/Cu(II) nanoparticles in the 500–4000 cm⁻¹ wave number range. The bands centered around 3400 cm⁻¹ and 1620 cm⁻¹ are, respectively, assigned to the O-H stretching and deforming vibrations of adsorbed water. For all samples,

Scheme 1. N-Arylation of nitrogen heterocycles with aryl halides in the presence of $Fe_3O_4@SiO_2/Ligand/Cu(II)$ nanocatalyst.

the absorption peak at $570-580 \text{ cm}^{-1}$ is observed, corresponding to the Fe–O vibration from the magnetite phase. $^{[42, 43]}$ The absorption bands of $780 \, \mathrm{cm}^{-1}$ and 1100 cm⁻¹ are assigned to symmetric and asymmetric stretching of Si-O-Si (Figure 1b), indicating that the magnetite NPs are successfully coated with silica layer.^[44] The FT-IR spectrum of Fe₃O₄@SiO₂-NH₂ emerged absorption $581 \, {\rm cm}^{-1}$ stretching peaks at (Fe–O, vibration), $1000-1150 \,\mathrm{cm}^{-1}$ (Si-O-Si, stretching vibration), $1400-1410 \text{ cm}^{-1}$ (C-N, stretching vibration), 1543 cm^{-1} (N–H, bending) and $2810-2986 \text{ cm}^{-1}$ (C–H, stretching vibration) (Fig. 1c). Also, the obvious bands with medium intensity in 3303 and 3351 cm⁻¹ regions are assigned to the N-H stretching from the successful immobilization of (3aminopropyl) triethoxysilane on the surface of the Fe₃O₄@SiO₂ NPs.^[42] From the FT-IR spectrum of Figure 1d, the peak at 1651 cm^{-1} belong to the stretching vibration mode of C = N (azomethine group) in Fe₃O₄@SiO₂/ligand, and another new band appears around 1712 cm^{-1} is due to stretching vibration of the C = O amide groups. The free ligand exhibits a $\nu(C=N)$ stretch at 1651 cm⁻¹ while in the complex, this band shifts to lower frequency and appears at 1628 cm⁻¹ due to the coordination of the nitrogen with the metal (Figure 1e).[42]

The structures and morphologies of the nanoparticles were characterized using transmission electron microscopy (TEM) (Figure 2a–c). The TEM image shows that the diameter of the pure Fe₃O₄ is uniform in a spherical morphology with an average diameter of 15 nm (Figure 2a).^[42] The Fe₃O₄ nanoparticles coated with SiO₂ revealed the increased diameter nearly to 25 nm in TEM image, which emphasize that Fe₃O₄ particles were completely covered with a uniform thin silica layer (Figure 2b). After successive coating with ligand complex of copper (II), these composites still maintained monodisperse with an average diameter of approximate 40 nm (Figure 2c).^[42]

The morphology of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂/ligand/Cu(II) NPs was also observed using FE-SEM (Figure 3a-c). The Fe₃O₄ nanoparticles are approximately spherical shapes with a smooth surface morphology (Figure 3a).^[42] The FE-SEM images indicate agglomerations of particles and the successful coating of the magnetic Fe₃O₄ particles (Figure 3b). Also, Figure 3c reveal that particles stay on their spherical shape even after Cu absorbance and forming Fe₃O₄@SiO₂/ligand/Cu(II) NPs.^[42]

Figure 3d-f show the particle size distributions of Fe_3O_4 , $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2/ligand/Cu(II)$ NPs. This size distribution is centered at a value of 14, 26 and 40 nm for Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2/ligand/Cu(II)$, respectively. The result is in good agreement with the size of particles shown in TEM images.

The energy dispersive X-ray spectroscopy (EDS) results, obtained from SEM analysis of $Fe_3O_4@SiO_2/ligand/Cu(II)$, are shown in Figure 4 and clearly show the presence of Cu in the catalyst. Moreover, the presence of Si, O and Fe signals indicates that the iron oxide particles are loaded into silica, and the higher intensity of the Si peak compared with the Fe peaks indicates that the Fe₃O₄ nanoparticles were





Scheme 2. Preparation process of Cu(II) complex functionalized Fe3O4@SiO2 nanoparticles^[42].

trapped by SiO_2 (Figure 4). According to the above analysis, it can be concluded that the $Fe_3O_4@SiO_2/ligand/Cu(II)$ has been successfully synthesized.

TGA curves were obtained to quantitatively determine the composition as well as the thermal stability of the magnetic catalyst (Figure 5A). The weight loss at temperatures below 150 °C could be attributed to water desorption from the surface of the samples.^[42] Also, the TGA curves of nanoparticles show a weight loss from 150 to 800 °C, resulting from the decomposition of organic compounds grafted to the Fe₃O₄@SiO₂ surface. As shown in Figure 5Ab, the TGA curve of Fe₃O₄@SiO₂/ligand/Cu(II) shows an initial weight loss of 4.1% below 150 °C, which might be due to the loss of adsorbed water. The mass loss of about 24.1% in the range of 150–800 °C is attributed to decomposition of the ligand and organic volatile compounds (Figure 5Ab). On the basis of these results, the successful functionalization of magnetic nanoparticles $Fe_3O_4@SiO_2$ with complex ligand of Cu(II) is verified.

The magnetic properties of the nanoparticles were characterized using a vibrating sample magnetometer (VSM). Neither coercivity nor remanence is observed, suggesting that the nanoparticles are superparamagnetic and $Fe_3O_4@SiO_2/ligand/Cu(II)$ nanoparticles and the catalyst after seven reaction cycle, have magnetization saturation values of 30.7 and 29.8 emu/g, respectively (Figure 5B). Therefore, these nanocomposites with high magnetization values can quickly respond to an external magnetic field and



IP cmastra (a) Fa Q (b) Fa Q (c) Fa Q

quickly redisperse once the external magnetic field is removed.

Then, in continuation of our interest in the application of magnetic nanocatalysts in organic synthesis,^[45, 46] we decided to explore *N*-arylation of nitrogen heterocycles with aryl halides in the presence of Fe₃O₄@SiO₂/Ligand/Cu(Π) catalyst.

For the initial optimization of the reaction conditions and the identification of the best conditions; iodobenzene and imidazole were chosen as model substrates. At the first stage, in order to elucidate the role of the catalyst, we found that in the absence of catalyst, the reaction did not proceed even at a high temperature (Table 1, entry1). As it can be seen, using of 0.6 mol% of Fe₃O₄@SiO₂/Ligand/Cu(Π) nanocatalyst in DMF afforded excellent yield of product in short reaction time (Table 1, entry 5). With catalyst amount increasing from 0.2 to 0.6 mol%, the yield increased from 49% to 94% (Table 1, entries 2–5). Further increase in the catalyst amount displayed no significant promoting effect on the yield, possibly due to the poor dispersion of the catalyst (Table 1, entry 6).

For showing the effect of the solvent, the same reaction was also carried out in different solvents, including DMF, NMP, DMSO, CH₃CN, toluene, THF and EtOH (Entries 5, 7–12) in the presence of 0.6 mol% of Fe₃O₄@SiO₂/Ligand/ Cu(Π) catalyst. As demonstrated in Table 1, the best result was obtained in DMF as solvent (Entry 5). Ullmann reactions are generally carried out in the presence of a base as a co-catalyst, which, apart from neutralizing the acidic byproducts formed during the reaction, increases the catalytic activity. Therefore, we next investigated the impact of a number of organic as well as inorganic bases such as Cs₂CO₃, NaOH, Et₃N, K₃PO₄ and K₂CO₃ under similar reaction conditions (Table 1, entries 5, 13–16). Under the



Figure 2. TEM images of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂ and (c) Fe₃O₄@SiO₂/ligand/Cu(II) NPs.



Figure 3. FE-SEM images of (a) Fe_3O_4 (b) Fe_3O_4 (c) Fe_3O_4 (c

described conditions at 100 °C in dimethylformamide, the best catalytic performance was obtained using Cs_2CO_3 (Table 1, entry 5). Table 1 shows the effect of the temperature on the model reaction yields using Fe₃O₄@SiO₂/Ligand/Cu(Π). It is obvious that the product yield increases notably with increasing temperature (Entries 5, 17–19) and the 1-phenyl-1*H*-imidazole can be obtained in 94% yield within 3.5 h at 100 °C (Entry 5). Therefore, 100 °C was the optimum temperature and all catalytic *N*-arylation reactions were carried out at this temperature.

Using these optimized reaction conditions, the efficiency of the catalyst was studied in the *N*-arylation of various aryl halides with a wide range of N(H)-heterocycles as the substrates. The summarized results in Table 2 clearly show appreciable product preparation in good to excellent yields for a wide array of aryl halides (iodides and bromides) bearing electron deficient and electron donating substituents in relatively short reaction times. However, the reaction of aryl halides substituted with electron-donating groups proceeded smoothly in longer reaction times with lower yields in comparison with electron-withdrawing groups. Furthermore,



Figure 4. EDS spectrum of Fe₃O₄@SiO₂/ligand/Cu(II) NPs.

various aryl halides such as iodobenzene and 2-iodopyridine were also coupled with phenylpiperazine efficiently under the optimized reaction conditions and the excellent yields were achieved (Entries 10, 11).

The applicability of this method for the coupling reaction of some aryl bromides with imidazole and 1H-benzimidazole was also examined (Table 2, entries 12–16). The examined aryl bromides underwent the coupling reactions and gave the desired products in good to excellent yields. However, the reaction proceeded in rather longer reaction times compared with aryl iodides. These results attest to the reliability of this catalyst for C–N coupling reactions.

In Table 3, the result for the coupling of *N*-arylation of iodobenzene with imidazole by this method is compared with some results from the literature with several Cu catalysts in Ullmann-type cross coupling reactions. Compared to most of the previously reported methods, the yield with the $Fe_3O_4@SiO_2/Ligand/Cu(II)$ catalyst is higher, the reaction temperature is lower and the reaction time is shorter. Moreover, the amount of the $Fe_3O_4@SiO_2/Ligand/Cu(II)$ catalyst required is much lower, and the turnover frequency (TOF) is higher, indicating the efficiency of this method.

Recyclability is a crucial parameter to evaluate the heterogeneity of a supported catalyst in organic synthesis. So the recyclability and reusability of $Fe_3O_4@SiO_2/Ligand/Cu(II)$ catalyst in the model reaction (reaction of iodobenzene with imidazole) was investigated. The reusability experiments results showed that catalytic activity did not decrease considerably after seven catalytic cycles (Figure 6a).

An attractive feature of heterogeneous catalysts is their easy separation from the reaction system. The $Fe_3O_4@SiO_2/$ Ligand/Cu(II) catalyst displayed a magnetization saturation value of 30.7 emu/g, indicating superparamagnetic behavior.^[42] Therefore, it ensured the rapid separation of the catalyst from the reaction system with the application of an external magnetic field (Figure 6b).

Also, by DLS analyses (Figure 6c), the average size of the catalyst nanoparticles was found to be 52 nm after seven reaction cycles. Furthermore, according to FE-SEM image (Figure 6d), after seven repeated reaction cycles, the



Figure 5. (A) Thermogravimetric analysis of (a) $Fe_3O_4@SiO_2-NH_2$ and $Fe_3O_4@SiO_2/ligand/Cu(II)$ NPs; (B) Magnetization curves for (a) $Fe_3O_4@SiO_2/ligand/Cu(II)$ nano-particles and (c) $Fe_3O_4@SiO_2/ligand/Cu(II)$ after seven reaction cycles.

Table 1. Screening reaction conditions for N-arylation of iodobenzene with imidazole.^a.

		Fe ₃ O ₄ @SiO Base, Solver				
Entry	Catalyst amount (mol%)	Solvent	Base	Temp (°C)	Time (h)	Yield (%) ^b
1	None	DMF	Cs ₂ CO ₃	140	12	0
2	0.2	DMF	Cs_2CO_3	100	8	49
3	0.4	DMF	Cs ₂ CO ₃	100	4	78
4	0.5	DMF	Cs ₂ CO ₃	100	4	91
5	0.6	DMF	Cs ₂ CO ₃	100	3.5	94
6	0.7	DMF	Cs ₂ CO ₃	100	3.5	92
7	0.6	NMP	Cs ₂ CO ₃	100	6	73
8	0.6	DMSO	Cs ₂ CO ₃	100	4	85
9	0.6	CH₃CN	Cs ₂ CO ₃	100	10	43
10	0.6	Toluene	Cs ₂ CO ₃	100	10	58
11	0.6	THF	Cs ₂ CO ₃	100	10	26
12	0.6	EtOH	Cs ₂ CO ₃	100	8	32
13	0.6	DMF	NaOH	100	8	63
14	0.6	DMF	Et₃N	100	10	24
15	0.6	DMF	K ₃ PO ₄	100	10	62
16	0.6	DMF	K ₂ CO ₃	100	7	74
17	0.6	DMF	Cs ₂ CO ₃	r.t	12	Trace
18	0.6	DMF	Cs ₂ CO ₃	80	6	84
19	0.6	DMF	Cs ₂ CO ₃	90	3.5	90
20	0.6	DMF	Cs ₂ CO ₃	110	3.5	93

^aReaction conditions: iodobenzene (1.0 mmol), imidazole (1.1 mmol), base (2 mmol), Fe₃O₄@SiO₂/Ligand/Cu(Π) catalyst, solvent (3 mL), open air. ^bIsolated yields.

morphology of the catalyst remained almost unaltered, except that the aggregation of the Cu nanoparticles might have occurred through the leaching/re-deposition phenomenon during the catalytic function.

In order to gain insight into the heterogeneous nature of catalyst, the hot filtration test was carried out. The model reaction was performed under optimized conditions and catalyst was quickly collected from the hot solution after 2 h and the reactants were allowed to undergo further reaction in the solution. According to GC analysis of the reaction mixture at different times, too small conversion of the reactants took place without catalyst. This result shows that the amount of leaching of the catalyst into the reaction mixture should be low and confirms that the catalyst acts heterogeneously in the reaction.

Also, to determine the content of copper ion in freshly catalyst and in each reaction cycle, the catalyst was removed by using a magnetic field and the copper amount in reaction medium after each reaction cycle was measured through Inductively Coupled Plasma (ICP) analyzer (Table 4). The analysis of the reaction mixture by the ICP technique showed that the amount of copper leaching was found to be 3.1% after the seven reaction run, which implies insignificant Cu leaching.

3. Conclusions

In conclusion, this study reports a ligand complex of Cu(II) supported on $Fe_3O_4@SiO_2$ magnetic heterogeneous nanoparticles, which show superior performance in the *N*-arylation of aryl halides by Ullmann-type cross coupling reaction without using external ligands or additives as promoters. This $Fe_3O_4@SiO_2/ligand/Cu(II)$ catalyst not only exhibits an impressive catalytic capacity to effect the *N*-arylation of

nitrogen heterocycles with aryl halides, but also possesses notable advantages such as high thermal stability, heterogeneous nature, easy preparation and easy separation of the catalyst. Also, the catalyst can be well dispersed in the reaction medium, easily magnetically recovered from the reaction mixture, and reused several times without significant loss of activity. Also, leaching test indicates that the catalytic reaction is mainly heterogeneous in nature. We hope that the present catalytic systems would be useful to synthesize industrially important organic compounds and synthetic starting materials in future.

4. Experimental

4.1. Materials and physical measurements

All chemicals were purchased from Aldrich and Merck in high purity. The reaction monitoring was performed by thin layer chromatography (TLC) on silica gel 60 F254 plates. All yields refer to isolated products. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus are uncorrected. The ¹H and ¹³C NMR spectra were obtained with a Bruker Avance DPX 250 MHz spectrometer (CDCl₃) using TMS as an internal standard. Transmission electron microscopy (TEM) images were taken on a Philips EM208 electronic microscope with an accelerating voltage of 100 kV. Field emission scanning electron microscopy characterization (FE-SEM) was performed on a Hitachi S-4160 at a 20 kV accelerating voltage and dynamic light scattering (DLS) were recorded on a HORIBALB550. The actual loading amount and leaching test of copper in the catalyst was analyzed by inductively coupled plasma spectrometry (ICP, Varian, Vista-pro). Elemental analyses were measured on a Thermofinigan Flash EA-1112 CHNSO

Entry	Substrate	N(H)-heterocycle	Product	Time (h)	Yield (%)
1	C ₆ H ₅ -I	Imidazole		3.5	94
2	4-NO ₂ -C ₆ H ₄ -I	Imidazole		2.5	96
3	4-Me-C ₆ H ₄ -I	Imidazole		5	92
4	C ₆ H ₅ -I	Indole		3	95
5	4-Me-C ₆ H₄-I	Indole	Me	5	90
6	C ₆ H ₅ -I	2-Methyl-indole		б	86
7	C ₆ H ₅ -I	Benzoimidazole		3	95
8	2-lodopyridine	Benzoimidazole		2	96
9	4-MeO-C ₆ H₄-I	Benzoimidazole	MeO	5	91
10	C ₆ H ₅ -I	1-Phenylpiperazine		4.5	85
11	2-lodopyridine	1-Phenylpiperazine		3.5	88
12	C ₆ H ₅ -Br	Imidazole		6	89
13	4-NO ₂ -C ₆ H ₅ -Br	Imidazole		4	94
14	2-Bromopyridine	Imidazole		4.5	93

(continued)

Table 2. Continued.

Entry	Substrate	N(H)-heterocycle	Product	Time (h)	Yield (%
15	4-Me-C ₆ H ₅ -Br	Imidazole	Me	6.5	86
16	2-Bromopyridine	Indole		4.5	96

^aReaction conditions: 1 mmol of aryl halides, 1.1 mmol of amine, 2 mmol of Cs₂CO₃, Fe₃O₄@SiO₂/Ligand/Cu(II) (0.6 mol%), DMF (3 ml), 100 °C. ^bIsolated yield.

 $\label{eq:comparing} \mbox{Table 3. Comparing the efficiency of various catalysts with $Fe_3O_4@SiO_2/Ligand/Cu(II)$ for the N-arylation of iodobenzene with imidazole.}$

Entry	Catalyst	Reaction Conditions	Time (h)	Yield (%)	TOF (h^{-1})	[Ref]
1	Fe ₃ O ₄ @SiO ₂ /Ligand/Cu(II) (0.015g, 0.6 mol%)	DMF, Cs ₂ CO ₃ , 100 °C	3.5	94	44.71	This work
2	CuFAP (0.1g, 12.5 mol%)	DMSO, K ₂ CO ₃ , 110 °C	6	92	1.23	[47]
3	Silica immobilized copper catalyst (5 mol%)	Toluene, Cs ₂ CO ₃ , 100 °C	8	92	2.30	[48]
4	CELL-Cu(0) (0.25g, 0.92 mol%)	DMSO, K ₂ CO ₃ , 130 °C	12	95	8.61	[49]
5	PANI-Cu (0.1g, 2.5 mol%)	CH ₃ CN, Cs ₂ CO ₃ , 80 °C	12	92	3.07	[50]
6	Cu-Y zeolite (10.8 mol%)	DMF, K ₂ CO ₃ , 120 °C	24	99	0.38	[51]
7	Cu ₂ O (10 mol%)	DMSO, KOH, 110 °C	24	90	0.37	[52]
8	Nano-CuO (2.5 mol%)	DMSO, KOH, 110 °C	24	91	1.52	[53]

rapid elemental analyzer. All products were characterized by spectra and physical data.

4.2. General procedure

4.2.1. Preparation of Fe₃O₄ MNPs

The Fe₃O₄ magnetic nanoparticles were synthesized based on the method reported by Javidi et al.^[54] FeCl₂.4H₂O (736 mg, 3.7 mmol), FeCl₃·6H₂O (2 g, 7.4 mmol) and polystyrene (PS 35000) (400 mg) were added to deionized water (30 mL) and stirred until the salts dissolved completely. Then, the transparent solution was heated at 80 °C with vigorous mechanically stirring under N₂ atmosphere for 30 min. Then 25% aqueous NH₃ was added dropwise with vigorous stirring to produce a black solid when the pH of reaction media reached 10. Then, the reaction mixture was cooled and the black magnetite nanoparticles were isolated by a permanent magnetic field, washed several times with distilled water, dried and calcined at 600 °C for 8 h.

4.2.2. Preparation of silica-coated MNPs (Fe₃O₄@SiO₂ MNPs)

The silica coated MNPs were synthesized according to our previous reports.^[42, 55] For the synthesis of $Fe_3O_4@SiO_2$, 0.1 g of the synthesized Fe_3O_4 nanoparticles were stirred in a mixture of deionized water (10 mL), ethanol (40 mL) and ammonia solution (1.5 mL, 25 wt%)) in a glass reactor for 60 min. Then, 2 mL of tetraethylorthosilicate (TEOS) was added into the solution under mechanical stirring. After stirring for 8 h at room temperature, the precipitate was collected from the solution using a magnet, and then washed several times with water and ethanol and dried at 60 °C for 6 h.

4.2.3. Synthesis of functionalized Fe₃O₄@SiO₂ nanoparticle with 3-(triethoxysilyl)-propylamine (Fe₃O₄@SiO₂-NH₂)

 $Fe_3O_4@SiO_2$ MNPs were modified with amino groups on the surface of SiO_2 through the siloxane linkage of 3-(triethoxysilyl)-propylamine. In a typical procedure, 0.5 g of $Fe_3O_4@SiO_2NPs$ was first dispersed in 5 mL ethanol containing 0.2 mL of 3-(triethoxysilyl)-propylamine (1 mmol), and then stirred under reflux conditions. After 12 h, the mixture is cooled to room temperature and $Fe_3O_4@SiO_2-NH_2$ magnetic nanoparticles were separated by magnetic decantation and washed three times with ethanol and distilled water, and finally dried at 80 °C for 6 h.

4.2.4. Preparation of Fe₃O₄@SiO₂ coated with ligand complex of copper (II) (Fe₃O₄@SiO₂/ligand/Cu(II))

To prepare the ligand functionalized Fe₃O₄@SiO₂ nanopar-(Fe₃O₄@SiO₂/ligand), a mixture of achieved ticles Fe₃O₄@SiO₂-NH₂ particles (0.5 g) and isatin (1 mmol, 0.147 g) in ethanol (10 mL) was stirred under reflux conditions for 16 h. The resulting product was separated using a magnet and thoroughly washed with deionized water and ethanol several times, and dried at 70 °C overnight giving the product Fe₃O₄@SiO₂/ligand. For the synthesis of the copper (II) complex functionalized Fe₃O₄@SiO₂ nanoparticles (Fe₃O₄@SiO₂/ligand/Cu(II)), Fe₃O₄@SiO₂/ligand (0.5 g) was added to 10 mL magnetically stirred solution of Cu(OAc)₂ (1 mmol,0.182 g) in ethanol and the resultant mixture was under reflux for 6h. The residue was collected by a magnet, followed by washing several times with ethanol and water to remove unreacted species and dried at 70 °C for 6 h.



Figure 6. (a) Recyclability of $Fe_3O_4@SiO_2/Ligand/Cu(II)$ in the synthesis of 1-phenyl-1*H*-imidazole under the optimized conditions; (b) Recoverability of the catalyst at the end of reactions by an external magnet; (c), (d) DLS and SEM images of $Fe_3O_4@SiO_2/Ligand/Cu(II)$ nanoparticles after seven reaction cycles.

Table 4. The	content	of Cu io	n in fres	hly catal	yst and	in each r	reaction	cycle. ^a .
Run	0	1	2	3	4	5	6	7
Content of Cu ion (mmol/g)	0.381	0.380	0.378	0.377	0.375	0.374	0.371	0.368

^aReaction conditions: iodobenzene (1.0 mmol), imidazole (1.1 mmol), Cs₂CO₃ (2 mmol), Fe₃O₄@SiO₂/Ligand/Cu(II) (0.6 mol%), DMF (3 ml), 100 °C.

4.2.5. General procedure for the N-arylation of aryl halides with amines

A 10 mL round-bottom flask was charged with aryl halide (1 mmol), amine (1.1 mmol), Cs_2CO_3 (2 mmol), DMF (3 mL), and $Fe_3O_4@SiO_2/Ligand/Cu(II)$ catalyst (0.6 mol%). The flask was stirred at 100 °C in air. The reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After the reaction was complete and separation of the catalyst with an external magnetic field, 15 mL of water and ethyl acetate were added. The organic phase was separated from the aqueous phase, which was extracted three times with ethyl acetate. The organic phases were collected together, dried over anhydrous Na_2SO_4 , and filtered. Then, the solvent was evaporated under reduced pressure to give the crude product. Ultimately, the pure products were isolated by chromatography on silica gel using mixture of hexane and ethyl acetate as eluent.

Selected spectral data

1-Phenyl-1*H*-imidazole (Table 2, entry 1)

Dark brown oil, ¹H NMR (250 MHz, CDCl₃): $\delta = 7.14-7.45$ (m, 7H), 7.80 (s, 1H); ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 118.2$, 121.4, 127.5, 129.9, 130.4, 135.5, 137.4.

1-Phenyl-1*H*-indole (Table 2, entry 4)

Dark brown oil, ¹H NMR (250 MHz, CDCl₃): $\delta = 6.59-6.63$ (m, 1H), 7.06–7.17 (m, 2H), 7.25–7.30 (m, 2H), 7.41–7.52 (m, 5H), 7.59–7.64 (m, 1H); ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 103.6$, 110.5, 120.4, 121.1, 122.4, 124.4, 126.4, 128.0, 129.3, 129.6, 135.8, 139.8; Anal. Calcd for C₁₄H₁₁N: C, 87.01; H, 5.75; N 7.25%. Found: C, 86.87; H, 5.89; N, 7.24%.

1-p-Tolyl-1H-indole (Table 2, entry 5)

Dark brown oil, ¹H NMR (250 MHz, CDCl₃): δ = 2.35 (s, 3H), 6.58 (dd, *J* = 4.2 Hz, 1H), 7.04–7.32 (m, 7 H), 7.43–7.47 (m, 1 H), 7.58–7.62 (m, 1H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 21.1, 103.2, 110.5, 120.1, 121.1, 122.2, 124.3, 128.1, 129.2, 130.1, 136.3, 137.3; Anal. Calcd for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76%. Found: C, 86.66; H, 6.48; N, 6.86%.

2-Methyl-1-phenyl-1H-indole (Table 2, entry 6)

Dark brown oil, ¹H NMR (250 MHz, CDCl₃): $\delta = 2.22$ (s, 3H), 6.32 (s, 1H), 7.00–7.07 (m, 3H), 7.25–7.29 (m, 2H), 7.36–7.51 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 13.4$, 101.3, 110.0, 119.6, 120.0, 121.0, 127.7, 128.0, 128.2, 129.4, 137.0, 138.2; Anal. Calcd for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76%. Found: C, 86.69; H, 6.42; N, 6.89%.

1-Phenyl-1H-benzimidazole (Table 2, entry 7)

Brown oil, ¹H NMR (250 MHz, CDCl₃): δ = 7.32–7.36 (m, 2H), 7.44–7.61 (m, 6H), 7.89-7.90 (m, 1H), 8.17 (s, 1H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 110.5, 120.6, 122.8, 123.7, 124.0, 128.0, 130.0, 136.3, 142.8, 144.2; Anal. Calcd for C₁₃H₁₀N₂: C, 80.39; H, 5.19; N, 14.42%. Found: C, 80.58; H, 5.03; N, 14.39%.

1-Pyridin-2-yl-1H-benzimidazole (Table 2, entry 8)

Brown oil, ¹H NMR (250 MHz, CDCl₃): δ = 7.26–7.39 (m, 3H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.86–7.93 (m, 2H), 8.06 (d, *J* = 7.8 Hz, 1 H), 8.58–8.62 (m, 2 H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 112.6, 114.3, 120.6, 121.8, 123.3, 124.2, 132.1, 138.9, 141.3, 144.7, 149.5, 149.9; Anal. Calcd for C₁₂H₉N₃: C, 73.83; H, 4.65; N, 21.52%. Found: C, 73.56; H, 4.73; N, 21.71%.

1,4-Diphenylpiperazine (Table 2, entry 10)

Dark brown solid, mp 150–151 °C, ¹H NMR (250 MHz, CDCl₃): δ = 3.36 (s, 8H), 6.88–7.02 (m, 6H), 7.28–7.34 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 49.5, 116.4, 120.1, 129.2, 151.3; Anal. Calcd for C₁₆H₁₈N₂: C, 80.63; H, 7.61; N, 11.75%. Found: C, 80.84; H, 7.55; N, 11.61%.

1-Phenyl-4-pyridin-2-ylpiperazine (Table 2, entry 11)

Light brown solid, mp 101–102 °C, ¹H NMR (250 MHz, CDCl₃): $\delta = 3.24$ (dd, $J^{l} = 7.0$ Hz, $J^{2} = 5.0$ Hz, 4H), 3.64 (t, J = 5.2 Hz, 4H), 6.56–6.65 (m, 2H), 6.79–6.93 (m, 3H), 7.18–7.25 (m, 2H), 7.40–7.47 (m, 1H), 8.14–8.16 (m, 1H); ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 45.3$, 49.2, 107.2, 113.6, 116.3, 120.1, 129.2, 137.6, 148.0, 151.3, 159.4; Anal. Calcd for C₁₅H₁₇N₃: C, 75.28; H, 7.16; N, 17.56%. Found: C, 75.44; H, 7.11; N, 17.45%.

2-Imidazol-1-ylpyridine (Table 2, entry 14)

Dark brown oil, ¹H NMR (250 MHz, CDCl₃): $\delta = 7.14-720$ (m, 2 H), 7.28-7.34 (m, 1H), 7.25-7.34 (m, 1H), 7.58 (s, 1H), 7.73-7.80 (m, 1H), 8.28 (s, 1H), 8.41-8.43 (m, 1H);¹³C NMR (62.9 MHz, CDCl₃): $\delta = 112.3$, 116.7, 122.0, 130.6, 132.2, 134.9, 139.0, 149.1; Anal. Calcd for C₈H₇N₃: C, 66.19; H, 4.86; N, 28.95%. Found: C, 65.99; H, 4.81; N, 29.20%.

Funding

Authors gratefully acknowledge the financial support of this work by the Research Council of University of Shiraz and University of Payame Noor.

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12 👄 S. ZAHMATKESH ET AL.

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