Application of γ-Fe_2O_3/talc/Cu^{II} NPs as a magnetic and heterogenous nanaocatalyst in carbon-sulfur cross-coupling reaction

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ABSTRACT

Herein a prominent, efficient, facile and environmentally benign catalytic activity of γ-Fe_2O_3/talc/Cu^{II} *NPs (as a superparamagnetic composite with average diameter of about 20-30 nm) has been shown in C-S cross-coupling reaction. A wide variety of aryl iodides, aryl bromides and aryl chlorides with electron-donating or electron-withdrawing substituents reacted with S8/thiourea towards corresponding diphenyl sulfides under eco-friendly and mild process conditions. The results demonstrated remarkable catalytic activity of the aforesaid nanostructured catalyst such as chemoselectivity and functional group tolerance.* γ-Fe_2O_3/talc/Cu^{II} *NPs as a magnetic catalyst was stable under reaction conditions and can be recycled at least five times with minimal loss of catalytic activity. Moreover, the use of commercially available and chemically stable sulfur transfer agent, eco-friendly and low-cost solvent and base as well as operational simplicity and easier work-up procedure make this method a promising candidate for potential applications in some organic reactions.*

Keywords: **γ-Fe_2O_3/talc/Cu^{II} NPs, aryl halide, C-S cross-coupling reaction, heterogeneous catalyst, ligand-free catalyst, WEB (Water Extract of Banana), green chemistry.**

1. *INTRODUCTION*

Organic molecules containing C-S bond (as the important reactive intermediates in organic chemistry) are prevalent in numerous bioactive natural products, pharmaceutical, and material science. [1-7] Thus, designing of efficient and high yield methods for synthesis of aryl sulfides and their derivatives have been developed over the last years due to their tremendous increasing applications in organic synthetic reactions. [8-12] Traditionally, C–S bond formation can be accomplished by the reaction of thiols with aryl/alkyl halides using various transition metals. [13-27] This classical method has attracted high attention as a great contribution to the recent growth of organic synthesis and indispensable tool for the synthetic chemists as well. Direct use of highly volatile, harmful, toxic, odorous, (in sometimes) expensive and less available thiols with high tendency to bind to transition metals can act as metal deactivators and leads to unavoidable environmental and safety problems. Moreover, in most of the C-S cross-coupling reactions, stable disulfides can be formed through easy oxidative homocoupling S–S reaction of thiols. [28-33] Consequently, the catalytic activity of transition metals in C-S cross-coupling reaction is less explored than the other cross-coupling reactions, [34-40] due to the disadvantages associated with these methods. To gain sustainable synthetic methods, instead of free thiols various sulfur reagents have been applied in the synthesis of various aryl sulfides and their derivatives such as: thiourea, [41-52] potassium thiocyanate, [53-56] carbon disulfide, [57-59] S8 [50,52,60-64] and sodium thiosulfate. [65] Among them, sulfur powder and also thiourea as low cost, odorless, safe and effective sulfur transfer agents show particular promise for C-S cross-coupling reaction. [42,66] A literature review reveals that amongst all the transition metals, copper is predominantly attractive because of its polarizability, special redox properties, low toxicity and cost effectiveness. [42,44,45,49,50,63,64,67]

Today with respect to the principle of green chemistry in both academia and industry, development of an environmentally friendly recyclable catalytic system devoid metal accumulations and organic waste generation is the main focus. In recent times, published reports indicate that researchers have interested in heterogeneous catalysts due to their economic and industrial significance. In this respect, immobilization of metals onto a magnetic support (heterogeneous metallic-based catalysts) with high surface area, easy product purification and reusability are highly preferred. [68-70] Recently, we disclosed the efficient catalytic activity of Cu^{II} attached to magnetic natural talc (γ-Fe_2O_3/talc/Cu^{II} NPs) as a stable and reusable magnetic nanostructured catalyst in preparation of 1H-pyrazolo[1,2-b] phthalazine-5,10-diones via one-pot multicomponent reaction. [71] Following this study, and in continuation of our sustainable approach for C-S cross-coupling reaction [50,51] herein, we report C-S cross-coupling reaction through the reaction of aryl halides with S_8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs.

2. Material and methods

2.1 Preparation of magnetic talc (γ-Fe_2O_3/ talc NPs)

The experiment was conducted at an ambient temperature and under a non-oxidizing oxygen-free environment through the flow of argon gas. A solution of $FeCl_3.6H_2O$ (7.4 mmol, 2.0 g,) and $FeCl_2.4H_2O$ (20.1 mmol, 4 g,) in 280 mL deionized water was added into a 500 mL three-necked flask equipped with argon gas inlet tube. After magnetically stirring the resulting solution for 30 min at room temperature, talc powder (8 g) was added. To impregnate the external surface of talc layers by metallic ions, the obtained suspension was stirred for 1 hour. Afterwards, under continuous stirring, 60 mL freshly prepared NaOH (2.0 M) was added drop by drop to the resulting suspension. After for 2 hours, the suspension was finally centrifuged, washed repeatedly in turn with ethanol and double distilled water. Then the obtained Fe_3O_4/ talc was sequentially dried (in a stove at 100 ℃ for 2 h), heated (in air at 2 ℃ min-1 up to 220 ℃) and kept in the furnace for 3 h to give γ-Fe_2O_3/talc NPs as reddish brown powder.

2.3. Preparation of Cu^{II} attached to magnetic natural talc (γ-Fe_2O_3/talc/Cu^{II} NPs)

The synthesized γ-Fe_2O_3/talc NPs (2 g) was added to a solution of $Cu(OAc)_2.H_2O$ (7 mmol, 1.4 g) in absolute methanol (20 mL). The resulting suspension was refluxed for 24 h. Afterwards, the obtained γ-Fe_2O_3/talc/Cu^{II} NPs was magnetically separated, washed repeatedly with water (2 × 50 mL) before drying at 100 °C for 12 h. The loading amount of Cu was 0.736 mmol per gram of γ-Fe_2O_3/talc/Cu^{II} NPs based on ICP-OES.

2.4. Typical procedure for preparation of diphenyl sulfide from the reaction of iodobenzene with S_8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs

γ-Fe_2O_3/talc/Cu^{II} NPs (1.1/1.4 mol%, 0.008/0.01g) was added to a refluxing solution of iodobenzene (1.0 mmol, 0.203 g), S_8/thiourea (0.5 mmol, 0.016 g/0.038 g) and WEB (water extract of banana peels ash) (1.0 mL) in EtOH (1.0 mL). Upon completion of the reaction (40/40 min), which was monitored by TLC, the reaction mixture was cooled to room temperature. The catalyst was separated by a magnetic field, washed with acetone (2×15 mL) and distilled water (4×15 mL) before drying at 100 ℃ for 2 h and reused for a consecutive run under the same reaction conditions. After evaporation of EtOH from the reaction mixture, the crude product was extracted with ethyl acetate (3×15 mL). Then the organic layer was dried over anhydrous Na2SO4 and concentrated by rotary evaporator. Afterwards, the crude product was purified by thin-layer chromatography on silica gel (n-hexane: ethyl acetate = 9: 1) to yield the desired product (diphenyl sulfide from S_8 (0.176 g, 95%) and thiourea (0.182 g, 98%)).

2.5. Preparation of WEB (water extract of banana peels ash)

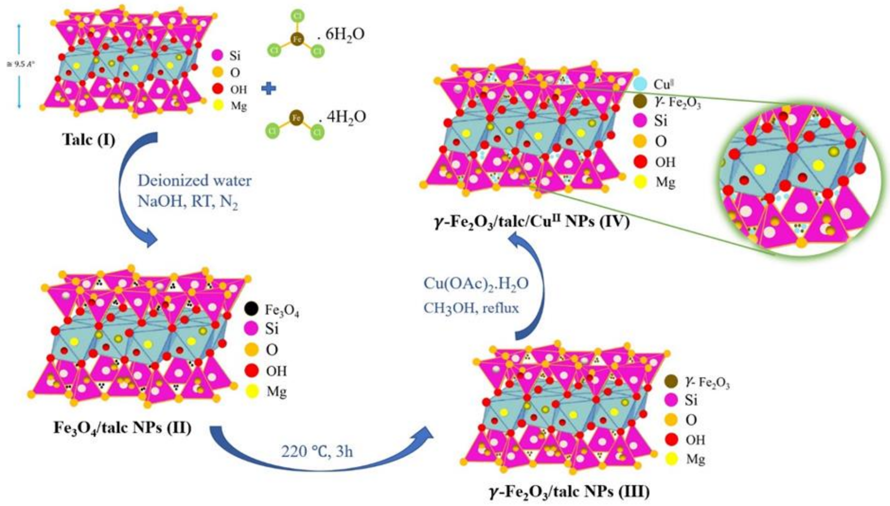
WEB (Water Extract of Banana) (scientific name: Musa balbisiana Colla; family: Musaceae; species: Musa balbisiana) was obtained according the method reported previously.[72] Initially, banana peels ash was obtained by the washed and dried the banana peels followed by burning it into ash. Then, the obtained banana ash (5 g) was suspended in distilled H_2O (100 mL), upon magnetically stirring for 10 min at room temperature. Finally, the resultant suspension was filtered through sintered glass crucible. The filtrate is termed WEB.

3. Results and discussion

3.1. Catalyst synthesis and characterization

Talc represented by a general formula of $Mg_3Si_4O_{10}(OH)_2$ [73] composed of an octahedral magnesium hydroxide sheet sandwiched between two tetrahedral silica sheets. All components of this 2:1 type layered configuration bonded together by ionic and covalent bonds. Talc as a monoclinic and/or triclinic mineral *without residual surface charge has Bronsted acidic sites due to the presence of few - SiOH and -MgOH groups on the lateral faces. On the other hand, the existence of Si-O-Si bonds on the basal surface displays low level of Lewis basicity. [74,75] Accordingly, it can be employed as an excellent natural support for various heterogeneous catalysts due to having chemically active sites. To provide easy separation of catalysts, using a simple magnetic bar (instead of centrifugation and filtration) from the reaction mixture, γ-Fe_2O_3 nanoparticles were incorporated into the talc structure. Furthermore, easy synthesis and functionalization, large surface area, high degree of chemical stability in various solvents as well as cost-effectiveness and biocompatibility have been achieved upon the application of magnetic nanoparticles in organic transformations. [76-80]*

By considering the importance of clean synthetic procedures and following our continuous interest in the development of efficient and environmentally friendly catalysts, [81,82] in the present study γ-Fe_2O_3/talc/Cu^{II} NPs was prepared from commercially available chemicals according the multiple steps in Scheme 1. [71] Talc powder (I) as promising supporting material were magnetized by reaction between Fe^{2+} and Fe^{3+} ions and NaOH. Thereafter, the obtained Fe_3O_4/talc was converted to γ-Fe_2O_3/talc NPs (II) upon heating at 220°C for 3 h. Then, the reaction of γ-Fe_2O_3/talc NPs with refluxing solution of $Cu(OAc)_2.H_2O$ in methanol produced Cu^{II} attached to magnetic natural talc (γ-Fe_2O_3/talc/Cu^{II} NPs (III)).



Scheme 1. The schematic pathway for the synthesis of Cu^{II} attached to magnetic natural talc (γ-Fe_2O_3/talc/Cu^{II} NPs).

Full characterization of γ-Fe_2O_3/talc/Cu^{II} NPs was performed by recording Fourier-transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD) analysis, transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray (EDX), EDX-mapping, vibrating sample magnetometer (VSM), and inductively coupled plasma optical emission spectrometry (ICP-OES).

To authenticate the structure of talc, (Figure1a) γ-Fe_2O_3/talc NPs (Figure 1b) and γ-Fe_2O_3/talc/Cu^{II} NPs (Figure 1c) Fourier transform infrared (FT-IR) spectroscopy was utilized. As it is evident from Figure 1a, the sharp absorption band at 3677 cm^{-1} could be attributed to symmetric stretching vibration of -SiOH and -MgOH groups on the lateral faces of talc. [83,84] In addition, the asymmetric and symmetric stretching vibrations of the Si-O-Si bond on the basal surface of talc were found at 1013 cm-1 and 669 cm^{-1}. [83,84] Also, the band at 466 cm^{-1} was indicative of the bending vibration of the Si-O-Si bond. [83,84] The vibrational frequencies of Mg-O bond (in octahedral layer) were appeared at 675 and 458 cm^{-1}. [83,84] (Figure 1a) Also, the presence of γ-Fe_2O_3 in the talc structure can be identified by the absorption band appeared at around 534 cm^{-1} corresponded the stretching vibration of Fe-O bond. [85] (Figure1b) In the FT-IR spectrum of γ-Fe_2O_3/talc/Cu^{II} NPs (Figure 1c) the coordination of $Cu(OAc)_2.H_2O$ to γ-Fe_2O_3/talc NPs has been proved by the presence of three absorption bands at 1592 cm^{-1}, 1441cm^{-1} and 451 cm^{-1} related to asymmetric and symmetric stretching vibrations of acetate ion as well as the stretching vibration of Cu-O bond.[86] It is worth noting that the latter absorption band is covered by the band attributed to the bending vibration frequency of Si-O-Si bond. Furthermore, this coordination can be verified by decreasing the intensity and frequency of the hydroxyl groups.

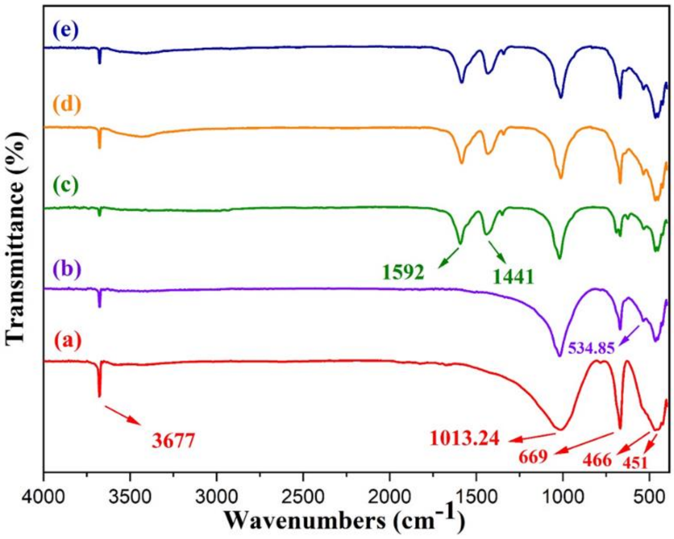


Figure 1. FT-IR spectra of the talc (a), γ-Fe_2O_3/talc NPs (b), γ-Fe_2O_3/talc/ Cu^{II} NPs (c), 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S_8/thiourea (d,e).

To study the phase purity and crystalline structure of γ-Fe_2O_3/talc NPs (Figure 2a), γ-Fe_2O_3/talc/ Cu^{II} NPs (Figure 2b) and 5th reused γ- Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S_8/thiourea, X-ray diffraction (XRD) patterns was utilized. As it is evident from Figure 2a, the characteristic peaks at 2θ = 30.27° (2 0 6), 35.7° (1 1 9), 53° (2 2 4), 57.4° (1 1 15) and 63° (4 0 12) are related to crystal structure of γ-Fe2O3. (Ref Code: 00-025-1402) Furthermore, three peaks at 2θ = 9.6° (0 0 1), 19.12° (0 0 2), 28.5° (0 0 3) recognized the crystallization of talc, which has an octahedral and tetrahedral structure. (Red Code: 04-010-7170) [84] Because of anchoring the Cu^{II} onto the magnetic natural talc, the hydrogen bonding was deformed, so the crystallinity value and intensity of all distinct peaks were decreased. The peak at 2θ = 43.52° (1 1 1) confirmed the presence of the Cu^{II} attached onto the γ-Fe_2O_3/talc NPs. (Ref Code: 00-004-0836) Afterall, the estimated crystalline size of γ-Fe_2O_3/talc/Cu^{II} NPs was about 24 nm, which calculated from Debye-Scherrer equation d= Kλ /(βcosθ).

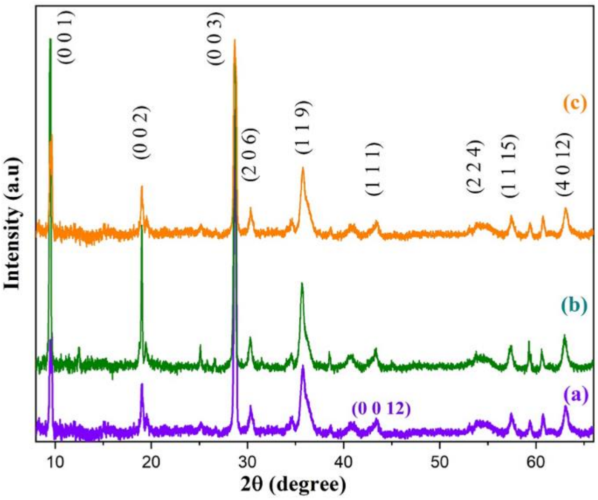


Figure 2. The XRD patterns of γ-Fe_2O_3 /talc NPs (a), γ-Fe_2O_3 /talc/Cu^{II} NPs (b), 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S_8(c).

Direct information about the structure, morphology and particle size of γ-Fe_2O_3/talc/Cu^{II} NPs was examined using transmission electron microscopy (TEM) analysis. Notably, Figure 3a represents the distribution of γ-Fe_2O_3 NPs inside the talc cavities. Furthermore, the distribution histograms of γ-

Fe_2O_3/talc/Cu^{II} NPs reveals that the average diameter of the nanoparticles is 20-30 nm (Figure 3b). The TEM results are in very good agreement with the results obtained from XRD (Figure 2).

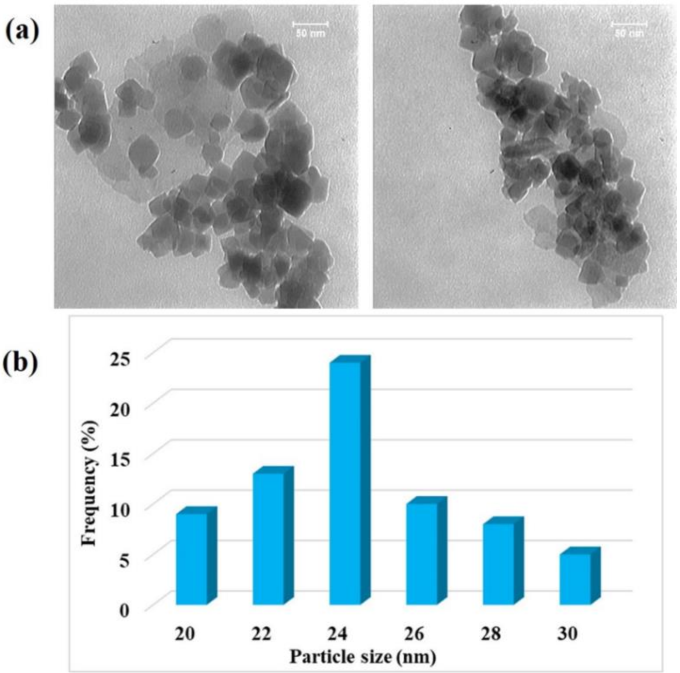


Figure 3. TEM images of γ-Fe_2O_3/talc/Cu^{II} NPs (a), Particle size distribution histogram of γ-Fe_2O_3/talc/Cu^{II} NPs (b).

The morphology of γ-Fe_2O_3/talc/Cu^{II} NPs was further investigated by field emission scanning electron microscopy (FE-SEM) technique. From Figure 4 it is evident that the as-synthesized nano structured catalyst exhibited good dispersity as well as an irregular and amorphous morphology.

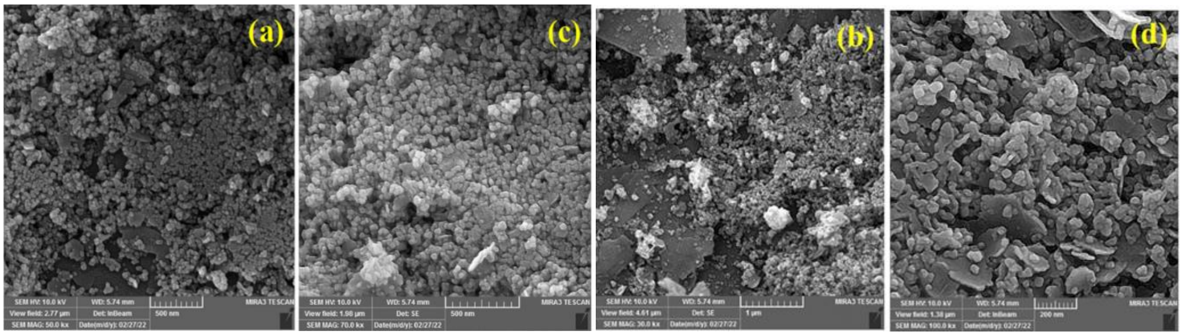


Figure 4. FE-SEM images of γ-Fe_2O_3/talc/Cu^{II} NPs (a and b), 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S_8(c and d).

Energy-dispersive X-ray (EDX) technique was applied to survey the types of elements present in the structure of γ-Fe_2O_3/talc/Cu^{II} NPs. According to the data shown in Figure 5a and Figure 5b the presence of Si, Mg, Fe, Cu and O evidently confirmed the catalyst composition. Furthermore, EDX-mapping analysis was performed to evaluate the elemental composition on the surface of nanostructured catalyst as depicted in Figure 5c. The presence of all elements (Si, O, N, Fe, C, and Cu) with uniform distributions was confirmed.

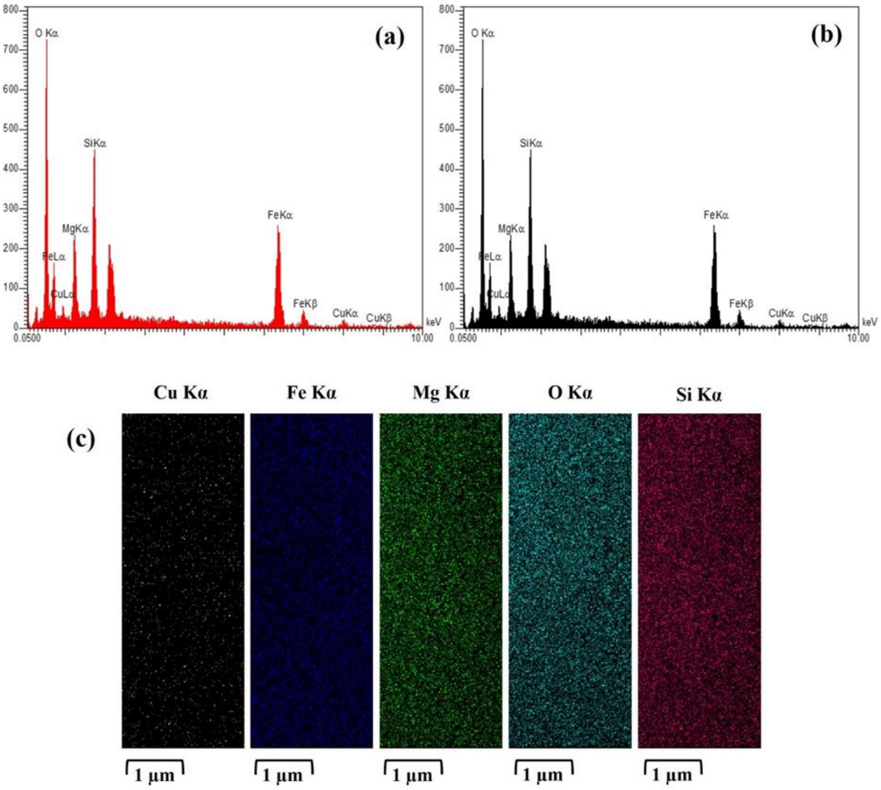


Figure 5. EDX spectrum of γ-Fe_2O_3/talc/Cu^{II} NPs (a), 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S_8 (b) and EDX-mapping analysis of γ-Fe_2O_3/talc/Cu^{II} NPs (c).

In the next phase, the magnetic property of γ-Fe_2O_3/talc/Cu^{II} NPs was determined using a vibrating sample magnetometer (VSM) analysis at room temperature. The easy separation of γ-Fe_2O_3/talc/Cu^{II} NPs by placing an external magnet experimentally represents the superparamagnetic nature of the nanostructured catalyst as can be seen from the magnetization curve in Figure 6. According to this analysis, the saturation magnetization value of γ- Fe_2O_3/talc/Cu^{II} NPs is estimated to be 12 emu g-1.

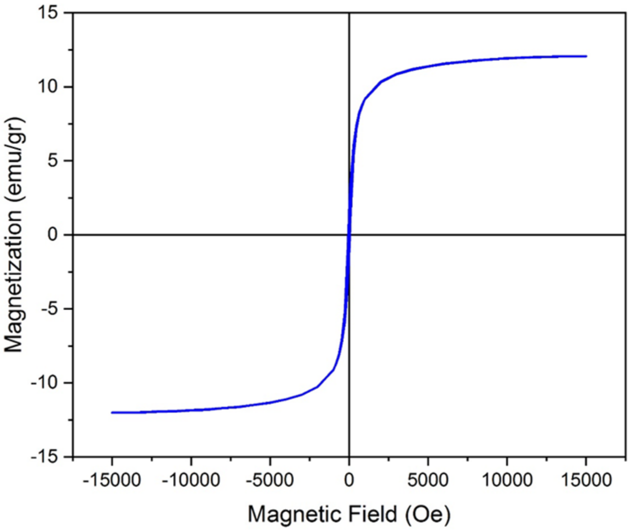


Figure 6. The magnetization curve of γ-Fe_2O_3/talc/Cu^{II} NPs.

3.2. Catalyst performance

The catalytic efficiency of γ-Fe_2O_3*/talc/*Cu^{II} *NPs in the C-S cross-coupling reaction was evaluated by the reaction between iodobenzene (1 mmol) and* S_8*/thiourea (0.5 mmol) as the source of sulfur.*

To determine the best reaction conditions, an intensive screening of reaction parameters was undertaken on model reaction. (Table 1) As replacement of hazardous solvents with relatively benign solvents in organic synthesis is one of the important aspects of green chemistry,[87] our initial study was started by performing the model reaction in EtOH due to environmental awareness. We and others have previously reported that "Water Extract of Banana" (WEB) can be used as base in Sonogashira-Hagihara and Suzuki-Miyaura cross-coupling reactions, Dakin oxidation as well as preparation of 2- amino-3,5-dicarbonitrile-6-thio-pyridines.[72,88-90] WEB contains potassium carbonate, sodium carbonate, potassium chloride, and sodium chloride as the major constituents along with other trace elements.[91] Accordingly and with respect to the principle of green chemistry, the sample reaction was examined using WEB as base. It could be seen that in the absence of γ-Fe2O3/talc/Cu^{II} *NPs and base, no product is detectable in refluxing EtOH even after a long period of time. (Table 1, entries 1-3) As evident from Table 1, the best results were obtained in short reaction time in the presence of γ-*Fe_2O_3*/talc/*Cu^{II} *NPs by using WEB. (Table 1, entry 4) The amount of catalyst loading has a considerable effect on the yield of the C-S cross-coupling reaction. To verify the effect of catalyst loading, in a set of experiments, the model reaction was conducted in the presence of different amounts of γ-*Fe_2O_3*/talc/*Cu^{II} *NPs. (Table 1, entries 5-8) Pleasantly, it was found that among various amounts of catalyst screened, the maximum yield of the desired product (in the reaction of iodobenzene with S8/thiourea) was obtained in 40/40 min by applying 1.1/1.4 mol% of catalyst. (Table 1, entries 6 and 4 respectively) It is apparent that the reasonable yield of the desired product (in the reaction of iodobenzene with* S_8*/thiourea) was achieved when the model reaction was performed in refluxing EtOH. (95/98 after 40/40 min) To achieve the best temperature, the model reaction's feasibility was examined at 70°C, and 65°C. (Table 1 entries 9,10) Evidently, the best catalytic activity of γ-*Fe_2O_3*/talc/*Cu^{II} *NPs was supplied in refluxing EtOH. (93/98 after 40/40 min) As the reaction was significantly affected by the amount of base, after finalizing the amount of catalyst loading and temperature for the reaction of iodobenzene with* S_8*/thiourea, the next target was to investigate the proper amount of WEB. (Table 1, entries 11,12) Applying 0.8 mL of WEB decreased the reaction yield to 70/62% even after 70/90 min, whereas additional amount of WEB up to 1.2 mL afforded the desired product as the same as using 1.0 mL of WEB. During our optimization studies, by applying the same reaction conditions, the model reaction was conducted in solvent-free condition. Comparatively, Table 1 shows that reaction was carried out but afforded lower yields even after long reaction time. (Table 1, entry13) In further attempts, to elucidate the catalyst's role in the C-S cross-coupling reaction, under the optimized reaction conditions the model reaction was examined in the presence of talc, γ-*Fe_2O_3*/talc NPs and* $Cu(OAc)_2.H_2O$ *as catalyst. (Table 1, entries 14-16) Reasonably, in all cases low yield of the desired product was obtained after prolonged reaction time. The obtained result in the presence of γ-*Fe_2O_3*/talc/*Cu^{II} *NPs confirmed much more efficiency of nanostructured catalyst than* $Cu(OAc)_2.H_2O$ *in the reaction of iodobenzene with S8/thiourea. (Table 1, entries 6 and 4 vs 16)*

Table1. Synthesis of diphenyl sulfide from the reaction of iodobenzene with S_8/thiourea catalyzed by γ-Fe_2O_3/talc/Cu^{II} NPs under different reaction conditions.

Entry	Catalyst (mol%) S_8/thiourea	Base ^{a} (mL)	Solvent	Temperature (°C)	Time(min) S_8/thiourea	Conversion (%) S_8/thiourea	Isolated yield (%) S_8/thiourea
1	-/-	-	EtOH	Reflux	24 (h)	0/0	0/0
2	-/-	WEB	EtOH	Reflux	24 (h)	0/0	0/0
3	1.4/1.4	-	EtOH	Reflux	24 (h)	0/0	0/0
4	1.4/**1.4**	**WEB**	**EtOH**	**Reflux**	25/**40**	100/**100**	98/**98**

5	1.2/1.2	WEB	EtOH	Reflux	30/50	100/100	95/90
6	**1.1**/1.1	**WEB**	**EtOH**	**Reflux**	**40**/65	**100**/100	**95**/80
7	0.97/0.97	WEB	EtOH	Reflux	60/80	100/100	80/75
8	2.7/2.7	WEB	EtOH	Reflux	20/35	100/100	90/85
9	1.1/1.4	WEB	EtOH	70	60/55	100/100	85/80
10	1.1/1.4	WEB	EtOH	65	65/65	100/100	80/75
11[b]	1.1/1.4	WEB	EtOH	Reflux	70/90	100/100	70/62
12[c]	1.1/1.4	WEB	EtOH	Reflux	40/40	100/100	90/90
13	1.1/1.4	WEB	-	74	24 /24(h)	40/40	35/35
14[d]	0.3g/0.3g	WEB	EtOH	Reflux	24 /24(h)	10/10	Trace/Trace
15[e]	0.3g/0.3g	WEB	EtOH	Reflux	24 /24(h)	10/10	Trace/Trace
16[f]	1.4/1.4	WEB	EtOH	Reflux	24 /24(h)	25/20	18/15

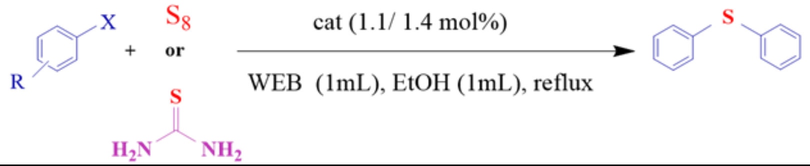
Reaction conditions: iodobenzene (1 mmol), S_8/thiourea (0.5 mmol). [a] The used base volume was 1.0 mL.[b] The used base volume was 0.8 mL.[c] The used base volume was 1.2 mL.[d] Reaction was performed in the presence of talc as the catalyst. [e] Reaction was performed in the presence of γ-Fe_2O_3/talc as the catalyst.[f] Reaction was performed in the presence of $Cu(OAc)_2.H_2O$ as the catalyst.

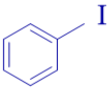
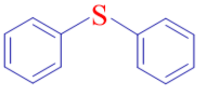
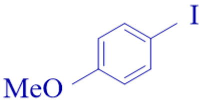
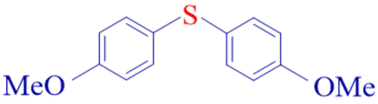
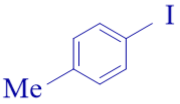
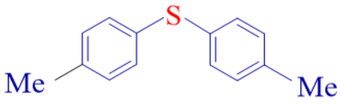
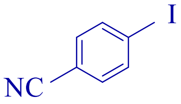
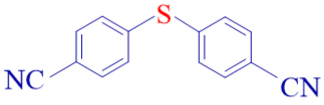
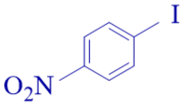
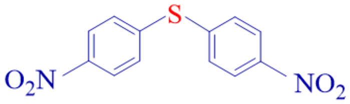
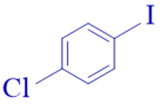
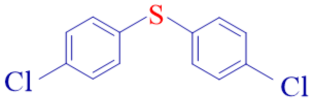
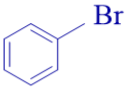
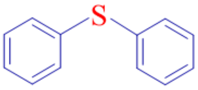
Having the established optimal reaction conditions (Table 1, entries 4 & 6), the scope of the present protocol was also extended to a wide variety of aryl halides bearing electron-donating and electron-withdrawing functional groups. (Table 2) As shown in Table 2, good to excellent yields of diaryl sulfides were obtained from the C-S cross-coupling reaction of differently substituted aryl iodides, aryl bromides and aryl chlorides with S8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs. It is worth noting that aryl halides containing electron-donating substituents (such as -OCH_3, -CH_3, -NH_2, -OH) required slightly longer reaction times than the other aryl halides containing electron-withdrawing substituents (such as -CN, -NO_2) to obtain the respective diaryl sulfides. (Table 2, entries 2,3, 8,13 and 14 vs entries 4,5 and 9) Comparatively, the lower reactivity of the electron-rich aryl halides is the result of more difficult insertion of copper into the carbon-halide bond than that of electron-poor ones. [92,93] As can be seen, the aryl iodides accomplished the C-S cross-coupling reaction more quickly than those by aryl bromides and aryl chlorides due to the lower C–I bond strength as compared to those of C–Br and C–Cl bonds. (Table 2 entry 1 vs entries 7 and 12) Interestingly, no N-arylating products were produced upon the reaction of aryl halides bearing unprotected amino groups with S8/thiourea using this catalytic system. (Table 2, entries 8 and 13) The reactions seemed to be effective in the case of 2-bromothiophene as a heteroaryl halide. The respective sulfide was afforded in an excellent yield under the optimized reaction conditions (Table 2, entry 10). The successful reaction of 1-bromonaphthalene to give the corresponding sulfide in a high yield could be regarded as an important aspect of this method. (Table 2, entry 11) It is important to note that the C-S cross coupling reaction is sensitive to the steric hindrance on the substrate. (Table 2, entries 15 and 16) The C-S cross-coupling reaction of 2,4-dinitro chlorobenzene with S8/thiourea produced the corresponding product in low yield (30%) even after long reaction time. (Table 2 entry 15) Additionally, after prolong reaction time no product was obtained in the case of 2-chloro aniline. (Table 2 entry 16).

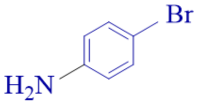
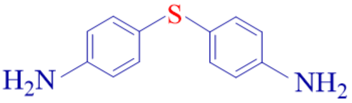
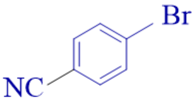
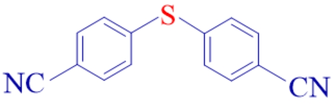
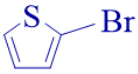
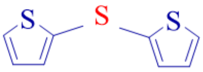
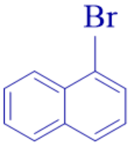
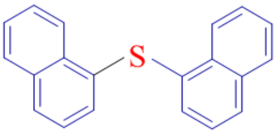
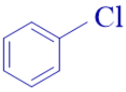
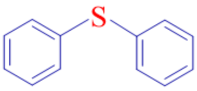
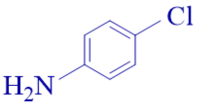
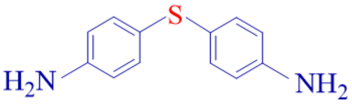
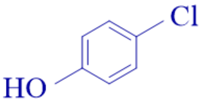
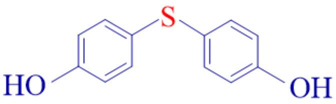
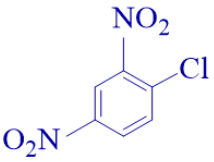
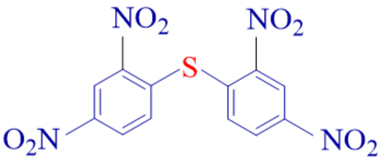
To extend the scope of the reaction further, the chemoselectivity of the present method was investigated. The mass spectrometry of the obtained product from the C-S cross-coupling reaction of 1-chloro-4-iodobenzene (as dihalogenated aryl halide) with S8/thiourea confirmed the more reactivity of iodide. (Table 2, entry 6) (Figure 9, Supporting Information file). Also, the NMR data confirmed the formation of diaryl sulfide in good to excellent yield as the only reaction product, and no diaryl disulfide was formed in any of the cases.

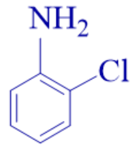
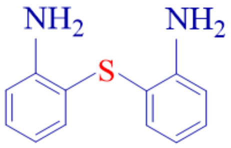
The progress of the C-S cross-coupling reaction was followed by the formation of respective product as well as the disappearance of aryl halide on TLC. All the obtained products were known which isolated and purified as oil or solid products. The synthesized compounds were initially identified by comparison of their melting points with those reported in the literature and/ or by mass spectrometry which the molecular ion peaks exhibited their respective m/z values. Also, the high-field ^1H NMR and ^{13}C NMR spectroscopy verified the structures of some selected products effectively.

Table 2. Synthesis of diaryl sulfides from the C-S cross-coupling reaction of aryl halides with S_8/thiourea catalyzed by γ-Fe_2O_3/talc/Cu^{II} NPs.



Entry	Aryl halide	Product	Time (h) S_8/thiourea	Conversion (%) S_8/thiourea	Isolated yield (%) S_8/thiourea
1			40 / 40(min)	100/100	95/98
2			1.35 / 1.35	87/75	85/72
3			1.15 / 2.10	89/80	85/75
4			40(min) / 2	95/92	91/89
5			40 / 40(min)	90/92	87/89
6			2.45 / 2.35	47/48	43/45
7			2.40 / 3	93/85	89/82

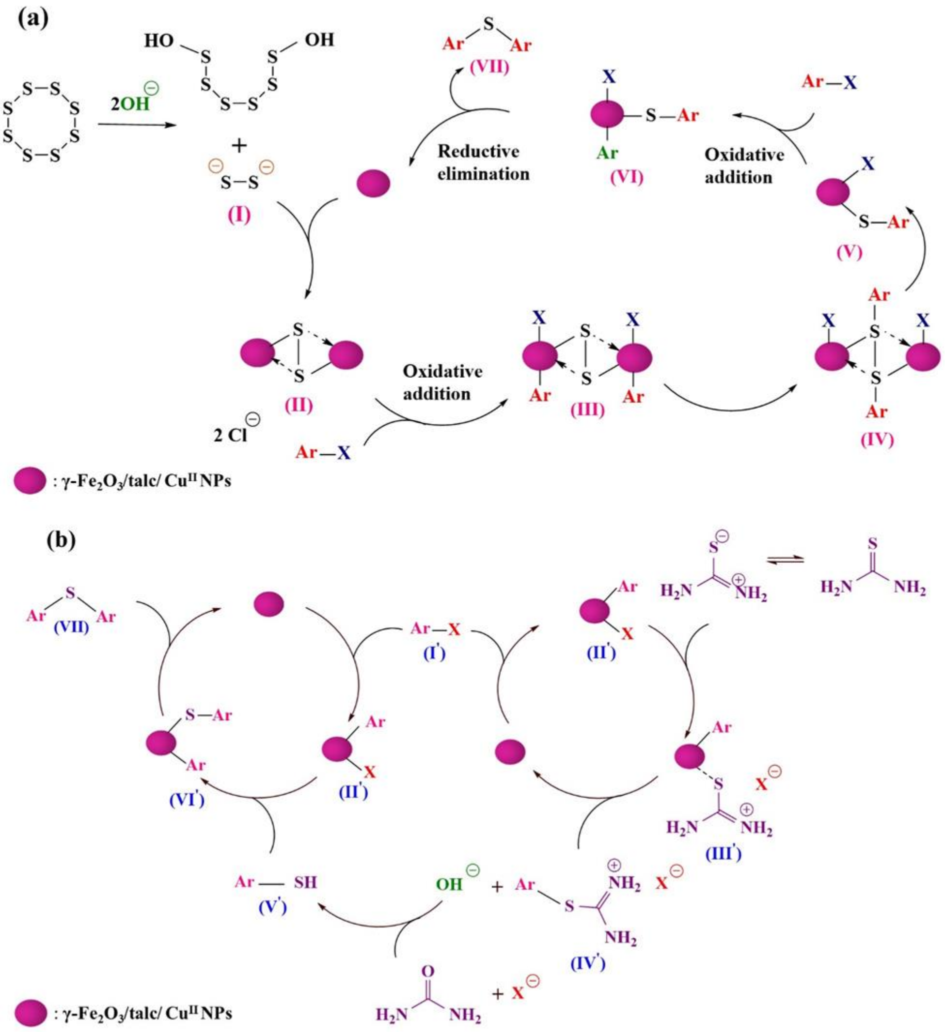
8			4.30 / 4.5	90/86	85/80
9			1.25 / 2.20	91/85	87/80
10			3.40 / 4.10	89/80	85/75
11			7.10 / 8.45	76/79	72/76
12			3 / 4	75/71	73/68
13			6.50 / 8.15	74/68	70/65
14			7.25 / 8.30	72/63	68/57
15			7.20 / 24 8 / 24	30/30 15/15	25/25

16			24 / 24	10/10	Trace/Trace

Consistent with the previously reported mechanism in the literature, [46,63] and according to our previous and present investigations [50,51], we would like to propose conceivable mechanism for the C-S cross-coupling reaction of aryl halides with S8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs in green media as shown in Scheme 2. Based on the literature report, it was found that WEB consists of potassium carbonate, sodium carbonate, potassium chloride, and sodium chloride as the major constituents along with a host of other trace elements.[91] The pH meter was used to determine the pH of WEB and it was found to be 9.8.

At the outset of the reaction of aryl halide with S_8, it was hypothesized that sulfur powder was converted to disulfide ion (I) in basic media which was instantly transformed to the stable copper disulfide (intermediate II) [63] in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs. Subsequently, III which was produced upon the oxidative addition reaction of aryl halide to intermediate II, generated the intermediate IV upon aryl migration reaction. Thereafter, the conversion of intermediate IV into V followed by oxidative addition reaction with another aryl halide molecule afforded the key intermediate VI. Ultimately, the desired diaryl sulfide (VII) was obtained through a reductive elimination reaction as well as the regeneration of the active catalytic species Cu^{II} for the next run. (Scheme 2a)

Also, a plausible mechanism of the reaction of aryl halides with thiourea was formulated, as shown in Scheme 2b. Primarily, it is supposed that via an oxidative addition reaction, Cu^{II} species insert into $C_{sp}{}^{2}$-X (I') bonds which produced the intermediate II'. Subsequently, intermediate III' was obtained upon the reaction of intermediate II' with thiourea. As shown in Scheme 2b, the reductive elimination of intermediate III' smoothly occurred to produce intermediate IV' and the γ-Fe_2O_3/talc/Cu^{II} NPs as well. In the following, the intermediate IV' afforded the thiol moiety (V') in alkaline media which reacted with another molecule of intermediate II' to give intermediate VI'. Finally, the desired diaryl sulfide (VII) was obtained through a reductive elimination manner on intermediate VI' alongside the regeneration of the active catalytic species Cu^{II} for the next run. To elucidate the details of the mechanism and scope of C-S cross-coupling reaction of aryl halide with S_8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs further investigations are required.



Scheme 2. Recommended mechanism pathway for the C-S cross-coupling reaction of aryl halides with S_8/thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs in green media.

3.2.1. Catalyst reusability

Nowadays, decreasing the chemical waste as well as improvement the selectivity and effectiveness of synthetic processes can be considered as one of the important criteria of chemical and pharmaceutical industries in a movement toward the green chemistry. To implement green chemistry principles development of recoverable and recyclable catalysts is necessary. In this regard, the recoverability and reusability of γ-Fe_2O_3/talc/Cu^{II} NPs in C-S cross-coupling reaction via the reaction of iodobenzene with S8/thiourea were investigated over five runs. The model reaction was performed under the optimized reaction conditions. Upon completion of the reaction (40/40 min), which was monitored by TLC, the reaction mixture was cooled to room temperature. The catalyst was separated by a magnetic field, washed with acetone (2×15 mL) and distilled water (4×15 mL) before drying at 100 °C for 2 h and applied for a consecutive run under the same reaction conditions. The results (Figure 7) showed that quantitative conversion/ isolated yield of desired product was obtained for five runs. Loss of activity of γ-Fe_2O_3/talc/Cu^{II} NPs was observed from the fifth run.

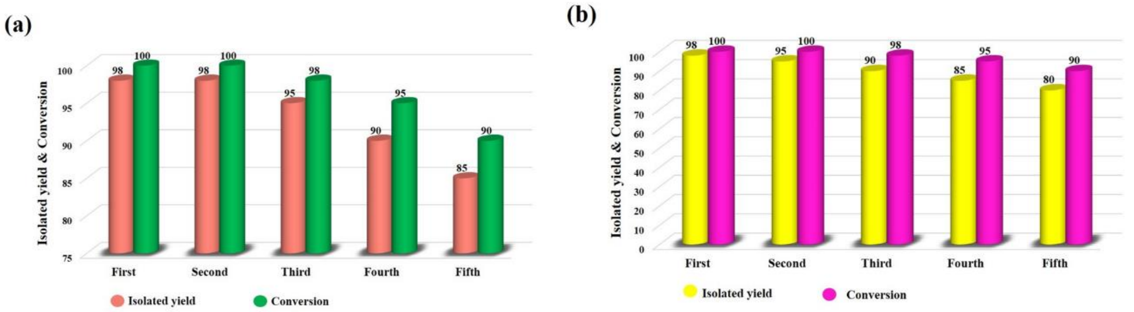


Figure 7. Recycling experiments of γ-Fe_2O_3/talc/Cu^{II} NPs in the reaction of iodobenzene with S_8 (a) and thiourea (b) under the optimized reaction conditions.

The structural stability of γ-Fe_2O_3/talc/Cu^{II} NPs after five cycles in the reaction of iodobenzene with S8/thiourea was investigated by FT-IR, XRD, FE-SEM, EDX and ICP-OES techniques.

No significant changes in the frequencies, intensities and shapes of absorption bands were observed in the FT-IR spectra of the 5th recovered γ-Fe_2O_3/talc/Cu^{II} NPs from the reaction of iodobenzene with S8/thiourea. (Figure 1d, 1e). Furthermore, XRD analysis of the 5th recovered catalyst demonstrated that the no changes were happened in the structure of γ-Fe_2O_3/talc/Cu^{II} NPs during the C-S cross-coupling reaction of iodobenzene with S8. (Figure 2c) Additionally, the average crystalline size of the 5th recovered γ-Fe_2O_3/talc/Cu^{II} NPs was estimated to be 24 nm according to the Debye-Scherrer equation. Additionally, according to the FE-SEM images depicted in Figure 4(c and d) no agglomeration was observed in the structure of 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs. Also, the presence of Si, Mg, Fe, Cu and O elements in the composition of 5th reused γ-Fe_2O_3/talc/Cu^{II} NPs clearly authenticated the composition stability of this nanostructured catalyst (Figure 5b). Based on ICP-OES analysis, the copper content of the fifth reused nanostructured catalyst from the reaction of iodobenzene with S8/thiourea is found to be 0.714/0.696 mmol g^{-1}, while the freshly-prepared catalyst was shown to contain 0.736 mmol of Cu per 1.000 g of γ-Fe_2O_3/talc/Cu^{II} NPs.

Now, the obtained results from FT-IR, XRD, FE-SEM, EDX and ICP-OES techniques confirms the stability of γ-Fe_2O_3/talc/Cu^{II} NPs in terms of functional groups, crystalline structure, morphology, particle size, and strong coordination of Cu^{II} ions to γ-Fe_2O_3/talc NPs even after five consecutive recycle runs.

3.2.2. Hot filtration test

Hot filtration test was performed to determine whether the catalyst is actually functioning in a heterogeneous manner. At the outset, the reaction of iodobenzene with S8/thiourea was conducted under the optimized reaction condition. When approximately 50% (after 20/20 minutes) of the reaction was proceeded (monitored by TLC) the catalyst was magnetically separated from the reaction medium. Then, the reaction was continued for another 20/20 minutes without any catalyst under the same reaction conditions and monitored by TLC. (Figure 8) It appeared that after 20/20 minutes in refluxing EtOH the reaction did not proceed further towards C-S cross-coupling reaction in the absence of γ-Fe_2O_3/talc/Cu_{II} NPs. It is apparent from the ICP-OES analysis

that a negligible amount of Cu leached out during the entire course of the catalytic C-S cross-coupling reaction (less than 0.07/0.07 mol%). It means that γ-Fe_2O_3/talc/Cu_{II} NPs has a truly heterogeneous nature and good stability without any significant leaching of Cu during the C-S cross-coupling reaction under the optimized reaction conditions.

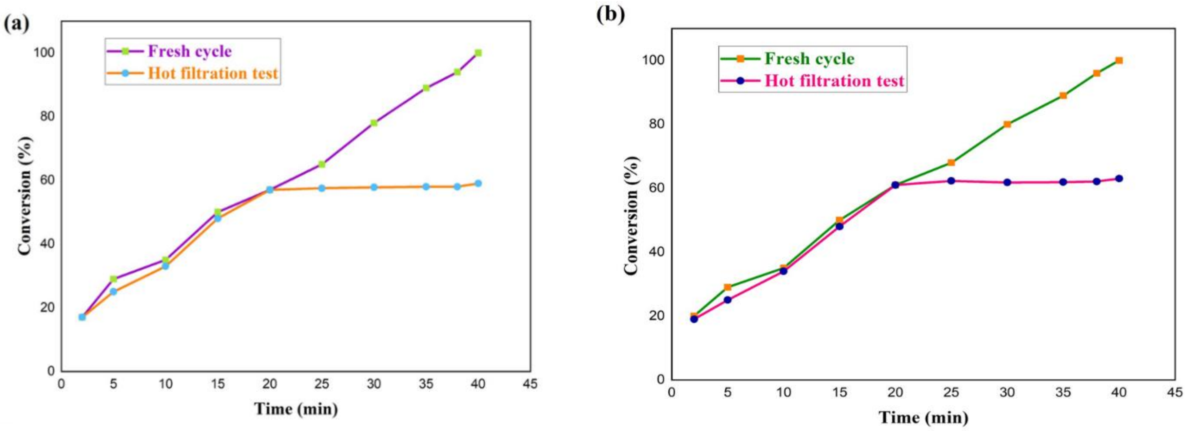


Figure 8. Time-dependent correlation of the product yield in the reaction of iodobenzene with S_8 (a) and thiourea (b) under the optimized reaction conditions.

3.2.3. Poisoning test

To further distinguish the true heterogeneity or homogeneity nature of catalysts, poisoning test was done under the optimized reaction conditions. For this purpose, in two separate flasks the reaction of iodobenzene with S8/thiourea was conducted in the presence and in the absence of ethylenediaminetetraacetic acid (EDTA) as an excellent scavenger of soluble Cu^{II} ions. [94] In this regard, the reaction progress was monitored by TLC. According to the obtained results, there is no noticeable difference between the yield of the reaction in the presence and absence of EDTA in spite of the high affinity of EDTA to form a stable complex with the soluble Cu^{II} ions. (Scheme 3). The obtained results demonstrated no leaching of Cu^{II} ions took place in solution during the reaction and the reaction arguably proceeds in a heterogeneous pathway. Therefore, the results clearly certified the pure heterogeneous nature of γ-Fe_2O_3/talc/Cu^{II} under the described reaction conditions. [Figure 9]

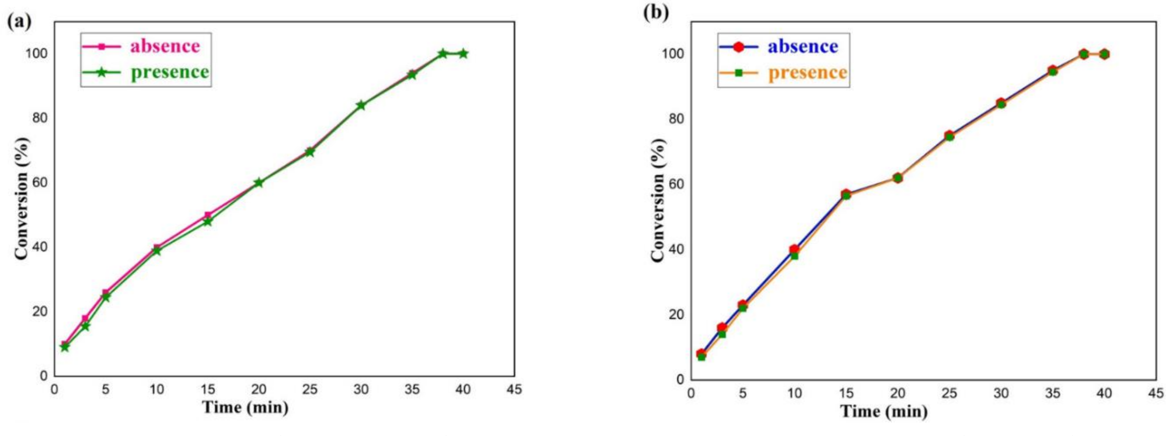


Figure 9. Product yield of the reaction of iodobenzene with S_8 (a) and thiourea (b) as a function of reaction time catalyzed by γ-Fe_2O_3/ talc/Cu^{II} NPs in the absence and the presence of EDTA.

In another variation, to show the unquestionable features of γ-Fe_2O_3/ talc/Cu^{II} NPs in C-S cross-coupling reaction of aryl halides with S8/thiourea, the efficiency of the present methodology was compared with some of the previously reported methods by others. The results of some commonly (homogeneous and heterogenous) catalysts in the literature for the same transformation were tabulated in Table 3 and Table 4. As can be apparently seen from Table 3 and Table 4 there is no doubt that all of the listed catalysts significantly improved the C-S cross-coupling reaction of aryl halides with S_8/thiourea, nevertheless the reaction of iodobenzene with S_8/thiourea in the presence of γ-Fe_2O_3/ talc/Cu^{II} NPs is much superior to almost all of the well-known catalyst systems in terms of solvent, (Table 3, entries 1-3 and 6, Table 4, entries 2-9 and 11)temperature, (Table 3 entries 1-7, Table 4, entries 1-11) reaction times, (Table 3, entries 2 and 5-7, Table 4, entries 2-9 and 11) easy recovering potential of the catalyst from the reaction mixture (Table 3, entries 1-4 *and 6-7, Table 4, entries 2-4 and 6-10) and high reusability as well. (Table 3 entries 6 -7, Table 4, entries 3-4, 6 and 8-9) Prominently, using environmentally friendly base (WEB) is another superiority of this catalytic methodology over the previously reported methods without using expensive catalyst, solvent and reagents.*

Table 3. Comparison of the catalytic activity of γ-Fe_2O_3/talc/Cu^{II} NPs with those of certain literature precedents using the C-S cross-coupling reaction of iodobenzene with S_8.

Entry	Catalyst	Base	Solvent	Temperature (°C)	Time(min)	Reusability	Isolated yield (%)	Ref.
1	NiO(II)-GO	NaOEt	DMSO	120	30	5	97	[52]
2	Ni(II)-SBA-15	KOH	DMSO	120	1.40 (h)	5	96	[61]
3	Cu(II)-Vanillin-MCM-41	KOH	DMSO	110	45	5	90	[62]
4	SBA-16/GPTMS-TSC-Cu^{I}[a]	KOH	-	110	20	7	98	[50]
5	$CuFe_2O_4$ MNPs	Cs_2CO_3	PEG-400	120	20.5 (h)	6	97	[63]
٦	CuI	$LiOH{\cdot}H_2O$	DMF	100	36 (h)	-	100	[64]
7	$Cu(OAc)_2$	Cs_2CO_3	PEG-200	110	7 (h)	-	100	[60]
8	γ-Fe_2O_3/talc/Cu^{II}	WEB	EtOH	Reflux	40	5	95	Present study

[a] Mesoporous SBA-16 functionalized by aminated 3-glycidyloxypropyltrimethoxysilane.

Table 4. Comparison of the catalytic activity of γ-Fe_2O_3/talc/Cu^{II} NPs with those of certain literature precedents using the *S*-arylation reaction with thiourea.

Entry	Catalyst	Base	Solvent	Temperature (°C)	Time(min)	Reusability	Isolated yield (%)	Ref.
1	Fe_3O_4@NiO/Co_3O_4	KOH	PEG-400	100	20	8	95	[51]
2	NiO(II)-GO	NaOEt	DMSO	120	4 (h)	5	95	[52]
3	CuI-DMAP[a]	K_2CO_3	DMSO	120	10 (h)	-	80	[42]
4	Pd_2dba_3-Triphos[b]	Cs_2CO_3	1,4-dioxane	100	18 (h)	-	71	[43]
5	CuO NPs	Cs_2CO_3	DMSO	110	15 (h)	4	97	[44]
6	CuO@GO	Cs_2CO_3	DMSO	110	12 (h)	-	98	[45]
7	Cu(II)-2-MPE[c]@MCM-41	KOH	DMF:H_2O	130	12 (h)	6	85	[46]
8	$Cu(OAc)_2.H_2O$	K_2CO_3	DMSO	120	12 (h)	-	94	[47]
9	CuI	Cs_2CO_3	DMSO	120	24 (h)	-	63	[49]
10	SBA-16/GPTMS-TSC[d] - Cu^{I}	KOH	-	110	60	7	95	[50]
11	Magnetic nano $CuFe_2O_4$	K_2CO_3	DMF	120	12 (h)	6	94	[48]
12	γ-Fe_2O_3/talc/Cu^{II}	WEB	EtOH	Reflux	40	5	98	Present study

[a] CuI- 4-Dimethylaminopyridine. [b] Tris(dibenzylideneacetone)dipalladium(0)/1,1,1-tris (diphenylphosphinomethyl)ethane. [c] 2-Methoxy-1- phenylethanone. [d] Mesoporous SBA-16 functionalized by aminated 3-glycidyloxypropyltrimethoxysilane with thiosemicarbazide.

4. Conclusion

In the present study, the application of the previously designed and characterized γ-Fe_2O_3/talc/Cu^{II} NPs as a superparamagnetic composite with average diameter of about 20-30 nm was attempted to expand in organic reactions. In this sense, a new efficient and eco-friendly procedure for the C-S cross-coupling reaction of aryl halides with S_8/thiourea under sustainable and mild process conditions is reported. The findings of the present study demonstrated the excellent performance of the chemically stable nanostructured catalyst in the coupling of differently substituted aryl halides (Cl, Br and I) with S_8/thiourea in green media using WEB as a non-hazardous and low-cost base. Moreover, significant features of the presented catalytic system are impressive catalytic activity, good to excellent yields of products, excellent functional group compatibility, *mild reaction conditions and easy experimental and work-up procedure. Given the magnetic nature, γ-Fe_2O_3/talc/Cu^{II} NPs showed great potential to be separated very simple by means of an external magnetic field and reused five times with only a slight decrease in its catalytic activity. It can be envisioned the advantage of the present method over existing ones for the C-S cross-coupling reaction of aryl halides with S_8/thiourea.*

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