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A green methodology for C–S cross-coupling reaction over Cu^{II} attached to magnetic natural talc (γ-Fe$_2$O$_3$/talc/Cu^{II} NPs) as a heterogeneous and ligand-free catalyst

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ABSTRACT

Herein a prominent, efficient, facile and environmentally benign catalytic activity of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs (as a superparamagnetic composite with average diameter of about 20-30 nm) has been shown in C–S cross-coupling reactions. A wide variety of aryl iodides, aryl bromides and aryl chlorides with electron-donating or electron-withdrawing substituents reacted with S$_8$ or thiourea forming the corresponding substituted diphenyl sulfides under eco-friendly and mild process conditions. The results demonstrated remarkable catalytic activity of the nanostructured catalyst such as chemoselectivity and functional group tolerance. γ-Fe$_2$O$_3$/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.
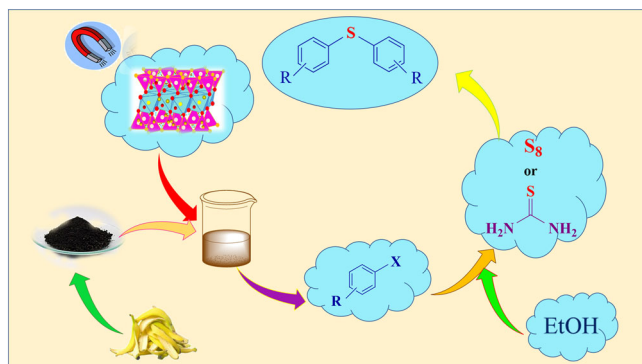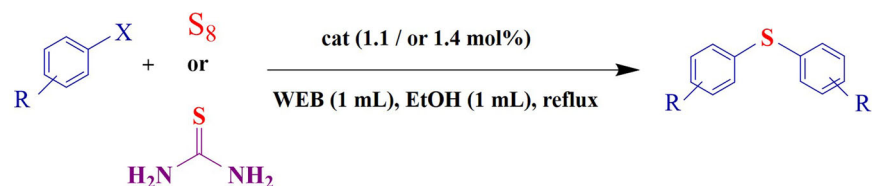
GRAPHICAL ABSTRACT

1. Introduction

Today, the carbon-heteroatom bond can be considered as one of the most important functional groups in organic synthesis which can be used as precursor or intermediate in the basic and vital infrastructures [1]. Over the last decades, organic molecules containing C–S bond (with a very special place in organosulfur chemistry), are prevalent in numerous bioactive natural products, pharmaceutical [2, 3], and material science [4–12]. Thus, designing efficient and high yield methods for the synthesis of aryl sulfides and their derivatives have been developed over the last years due to their increasing applications in organic synthetic reactions [13–20]. Traditionally, C–S bond formation can be accomplished by the reaction of thiols with aryl/alkyl halides using various transition metals [20–34]. 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 a 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 [35–40]. Consequently, the catalytic activity of transition metals in C–S cross-coupling reaction is less explored than the other cross-coupling reactions [1, 41–46], due to the disadvantages associated with these methods. To gain sustainable synthetic methods, instead of free thiols various

Scheme 1. Diphenyl sulfides preparation from the reaction of aryl halides with S_8 or thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs in green media.

sulfur reagents have been applied in the synthesis of various aryl sulfides and their derivatives such as: thiourea [47–58], potassium thiocyanate [59–62], carbon disulfide [63–65], S_8 [56,58,66–70] and sodium thiosulfate [71]. 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 [48, 72]. 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 [48, 50, 51, 55, 56, 69, 70, 73]. Also, in the area of transition-metal catalyzed reactions, copper with quite different behavior sometimes competes with palladium which may be considered as a simple renaissance of Ullmann's chemistry [74–81]. Most of the widely used copper derivatives with homogeneous nature, (such as salts, oxides, or complexes with ligands) hampers the recovery, reuse as well as their practical applicability mainly in the synthesis of drug molecules, which must be free of any residual metal [81–84].

Consequently, with respect to the principle of green chemistry in both academia and industry, development of an environmentally friendly heterogeneous copper catalytic system devoid metal accumulations, organic waste generation as well as their economic and industrial significance, is the main focus in recent years [77, 79, 85–88]. Heterogeneous catalysts with the benefits of recovery and reuse after completion of the green chemical processes also has some disadvantages such as highspeed centrifugation step or tedious workup procedures, which need to be overcome by more developed techniques. Magnetic nanoparticles have been widely used in designing environmentally friendly heterogeneous nanostructured catalysts due to their super magnetism, large surface areas as well as non-toxicity. An outstanding feature of magnetic nanostructured catalysts is that they can be easily separated from the reaction mixture by an external magnetic field, which achieves a simple separation of the catalyst without using filtration or centrifugation. Moreover, magnetic nanoparticles provide high potential active sites for immobilization of metal ions. There are many examples in the literature about the utility of heterogeneous copper-based catalysts in cross-coupling reactions. Most of them based on copper complexes with functionalized ligands immobilized on different supports [89–96]. Synthesis of specialized ligands, immobilization and copper complex formation steps, often, may limit the application of catalyst in organic reactions. In this respect, immobilization of metals onto a ligand free magnetic support

(heterogeneous metallic-based catalysts) with high surface area, easy product purification and reusability are highly preferred [97–99]. 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 ligand free magnetic nanostructured catalyst in preparation of 1*H*-pyrazolo[1,2-b] phthalazine-5,10-diones *via* one-pot multicomponent reaction [100]. Following this study, and in continuation of our sustainable approach for C–S cross-coupling reaction [56, 57] herein, we report C–S cross-coupling reaction through the reaction of aryl halides with S_8 or thiourea in the presence of γ-Fe_2O_3/talc/Cu^{II} NPs (Scheme 1).

2. Results and discussion

2.1. Catalyst synthesis and characterization

Talc represented by a general formula of $Mg_3Si_4O_{10}(OH)_2$ [101] was composed of an octahedral magnesium hydroxide sheet sandwiched between two tetrahedral silica sheets. All components of this 2:1 type layered configuration were bonded together by ionic and covalent bonds. Talc as a monoclinic and/or triclinic mineral without residual surface charge has BrØnsted 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 [102–104]. Accordingly, talc 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 [105–109].

By considering the importance of clean synthetic procedures and following our continuous interest in the development of efficient and environmentally friendly catalysts [110, 111], in the present study γ-Fe_2O_3/talc/Cu^{II} NPs was prepared from commercially available chemicals according the multiple steps in Figure S36 (Supplemental Materials) [100]. 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

Table 1. Synthesis of diphenyl sulfide from the reaction of iodobenzene with S_8 or thiourea catalyzed by γ-Fe$_2$O$_3$/talc/Cu^{II} NPs under different reaction conditions.

Entry	Catalyst (mol%)S_8 or thiourea	Basea (mL)	Solvent	Temperature (°C)	Time(min)S_8 or thiourea	Conversion (%)S_8 or thiourea	Isolated yield (%) S_8 or thiourea
1	–/–	–	EtOH	Reflux	24 (h)	0 / or 0	0 / or 0
2	–/–	WEB	EtOH	Reflux	24 (h)	0 / or 0	0 / or 0
3	1.4 / or 1.4	–	EtOH	Reflux	24 (h)	0 / or 0	0 / or 0
4	1.4 / or **1.4**	**WEB**	**EtOH**	**Reflux**	25 / or **40**	100 / or **100**	98 / or **98**
5	1.2 / or 1.2	WEB	EtOH	Reflux	30 / or 50	100 / or 100	95 / or 90
6	**1.1** / or 1.1	**WEB**	**EtOH**	**Reflux**	**40** / or 65	**100** / or 100	**95** / or 80
7	0.97 / or 0.97	WEB	EtOH	Reflux	60 / or 80	100 / or 100	80 / or 75
8	2.7 / or 2.7	WEB	EtOH	Reflux	20 / or 35	100 / or 100	90 / or 85
9	1.1 / or 1.4	WEB	EtOH	70	60 / or 55	100 / or 100	85 / or 80
10	1.1 / or 1.4	WEB	EtOH	65	65 / or 65	100 / or 100	80 / or 75
11b	1.1 / or 1.4	WEB	EtOH	Reflux	70 / or 90	100 / or 100	70 / or 62
12c	1.1 / or 1.4	WEB	EtOH	Reflux	40 / or 40	100 / or100	90 / or 90
13	1.1 / or 1.4	WEB	–	74	24 / or 24(h)	40 / or 40	35 / or 35
14d	0.3g / or 0.3 g	WEB	EtOH	Reflux	24 / or 24(h)	10 / or 10	Trace / or Trace
15e	0.3g / or 0.3 g	WEB	EtOH	Reflux	24 / or 24(h)	10 / or 10	Trace / or Trace
16f	1.4 / or 1.4	WEB	EtOH	Reflux	24 / or 24(h)	25 / or 20	18 / or 15

Reaction conditions: iodobenzene (1 mmol), S_8 or thiourea (0.5 mmol). The first and the second numbers are related to the S_8 reactions' data and the thiourea reactions' data, respectively. [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$_2$O$_3$/talc as the catalyst. [f]Reaction was performed in the presence of Cu(OAc)$_2$.H$_2$O as the catalyst. The optimized conditions of the S_8 reactions' data and the thiourea reactions' data are represented in bold in rows 4 and 6, respectively.

γ-Fe$_2$O$_3$/talc NPs (II) upon heating at 220 °C for 3 h. Then, the reaction of γ-Fe$_2$O$_3$/talc NPs with refluxing solution of Cu(OAc)$_2$.H$_2$O in methanol produced Cu^{II} attached to magnetic natural talc (γ-Fe$_2$O$_3$/talc/Cu^{II} NPs (III)).

Full characterization of γ-Fe$_2$O$_3$/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) (Supplemental Materials, Figures S1–S6).

2.2. Catalyst performance

The catalytic efficiency of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs in the C-S cross-coupling reaction was evaluated by the reaction between iodobenzene (1 mmol) and S_8 or thiourea (0.5 mmol) as the source of sulfur. To determine the best reaction conditions, an intensive screening of reaction parameters was undertaken on a 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 [112], our initial study was started by performing the model reaction in EtOH. We and others have previously reported that "Water Extract of Banana" (WEB) can be used as a 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 [113–116]. WEB contains potassium carbonate, sodium carbonate, potassium chloride, and sodium chloride

as the major constituents along with other trace elements [117]. 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-Fe$_2$O$_3$/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). The best results were obtained in short reaction time in the presence of γ-Fe$_2$O$_3$/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$_2$O$_3$/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 S_8 or thiourea) was obtained in 40/or 40 min by applying 1.1/or 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 or thiourea) was achieved when the model reaction was performed in refluxing EtOH. (95%/or 98% after 40/or 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$_2$O$_3$/talc/Cu^{II} NPs was supplied in refluxing EtOH. (93%/or 98% after 40/or 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 or 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%/or 62% even after 70/or 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$_2$O$_3$/talc NPs and Cu(OAc)$_2$.H$_2$O 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$_2$O$_3$/talc/Cu^{II} NPs confirmed much more efficiency of nanostructured catalyst than Cu(OAc)$_2$.H$_2$O in the reaction of iodobenzene with S$_8$ or thiourea (Table 1, entries 6 and 4 vs 16).

Having the established optimal reaction conditions (Table 1, entries 4 and 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 S$_8$ or thiourea in the presence of γ-Fe$_2$O$_3$/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 [118, 119]. 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 S$_8$ or 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 S$_8$ or 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).
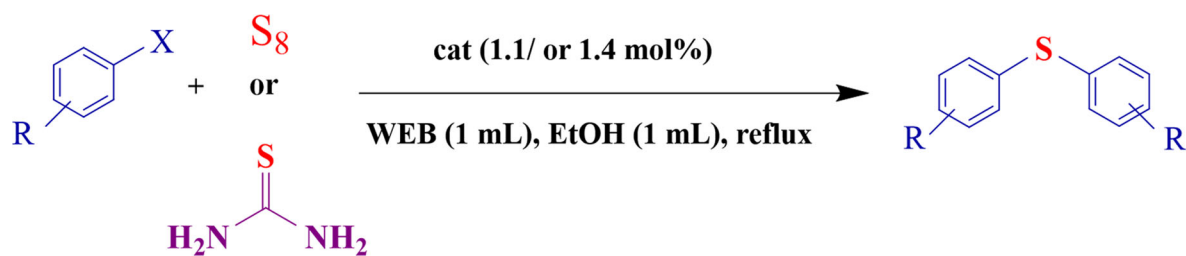
To extend the scope of the reaction further, the chemoselectivity of the present method was investigated. The mass spectrometry of the obtained product from the C–S cross-coupling reaction of 1-chloro-4-iodobenzene (as dihalogenated aryl halide) with S$_8$ or thiourea confirmed the more reactivity of iodide (Table 2, entry 6) (Figure S26). 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 ^{1}H NMR and ^{13}C NMR spectroscopy verified the structures of some selected products effectively (Supplemental Materials, Figures S11–S35).

Consistent with the previously reported mechanism in the literature [52, 69], and according to our previous and present investigations [56, 57], we would like to propose conceivable mechanism for the C–S cross-coupling reaction of aryl halides with S$_8$ or thiourea in the presence of γ-Fe$_2$O$_3$/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 [117]. 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) [69] in the presence of γ-Fe$_2$O$_3$/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).
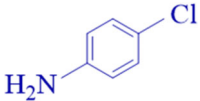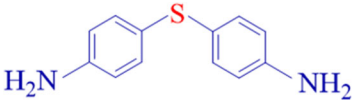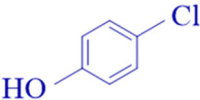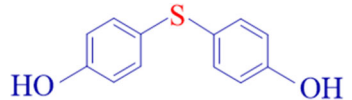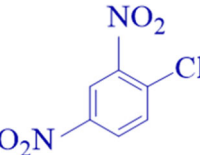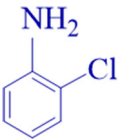
Also, a plausible mechanism of the reaction of aryl halides with thiourea was formulated, as shown in Scheme 2b. Primarily, it is supposed that via an oxidative addition reaction, Cu^{II} species insert into C$_{SP}^2$-X (I′) bonds which produced the intermediate II′. Subsequently, intermediate III′ 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$_2$O$_3$/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

Table 2. Synthesis of diaryl sulfides from the C–S cross-coupling reaction of aryl halides with S_8 or thiourea catalyzed by γ-Fe$_2$O$_3$/talc/Cu^{II} NPs.

Entry	Aryl halide	Product	Time (h)S_8 or thiourea	Conversion (%)S_8 or thiourea	Isolated yield (%)S_8 or thiourea
1			40 / or 40(min)	100 / or 100	95 / or 98
2			1.35 / or 1.35	87 / or 75	85 / or 72
3			1.15 / or 2.10	89 / or 80	85 / or 75
4			40(min) / or 2	95 / or 92	91 / or 89
5			40 / or 40(min)	90 / or 92	87 / or 89
6			2.45 / or 2.35	47 / or 48	43 / or 45
7			2.40 / or 3	93 / or 85	89 / or 82
8			4.30 / or 4.5	90 / or 86	85 / or 80
9			1.25 / or 2.20	91 / or 85	85 / or 80
10			3.40 / or 4.10	89 / or 80	85 / or 75
11			7.10 / or 8.45	76 / or 79	72 / or 76
12			3 / or 4	75 / or 71	73 / or 68

(continued)

Table 2. Continued.

Entry	Aryl halide	Product	Time (h)S$_8$ or thiourea	Conversion (%)S$_8$ or thiourea	Isolated yield (%)S$_8$ or thiourea
13	(4-chloroaniline)	(bis(4-aminophenyl) sulfide)	6.50 / or 8.15	74 / or 68	70 / or 65
14	(4-chlorophenol)	(bis(4-hydroxyphenyl) sulfide)	7.25 / or 8.30	72 / or 63	68 / or 57
15*	(1-chloro-2,4-dinitrobenzene)	(bis(2,4-dinitrophenyl) sulfide)	7.20/24 8/24	30/30 15/15	25/25 10/10
16	(2-chloroaniline)	(bis(2-aminophenyl) sulfide)	24 / or 24	10 / or 10	Trace / or Trace

The first and the second numbers are related to the S$_8$ reactions' data and the thiourea reactions' data, respectively. *The data of the first and the second lines are related to the S$_8$ reaction (after 7.20 h to 24 h) and the thiourea reaction (after 8 h to 24 h), respectively.

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$_8$ or thiourea in the presence of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs further investigations are required.
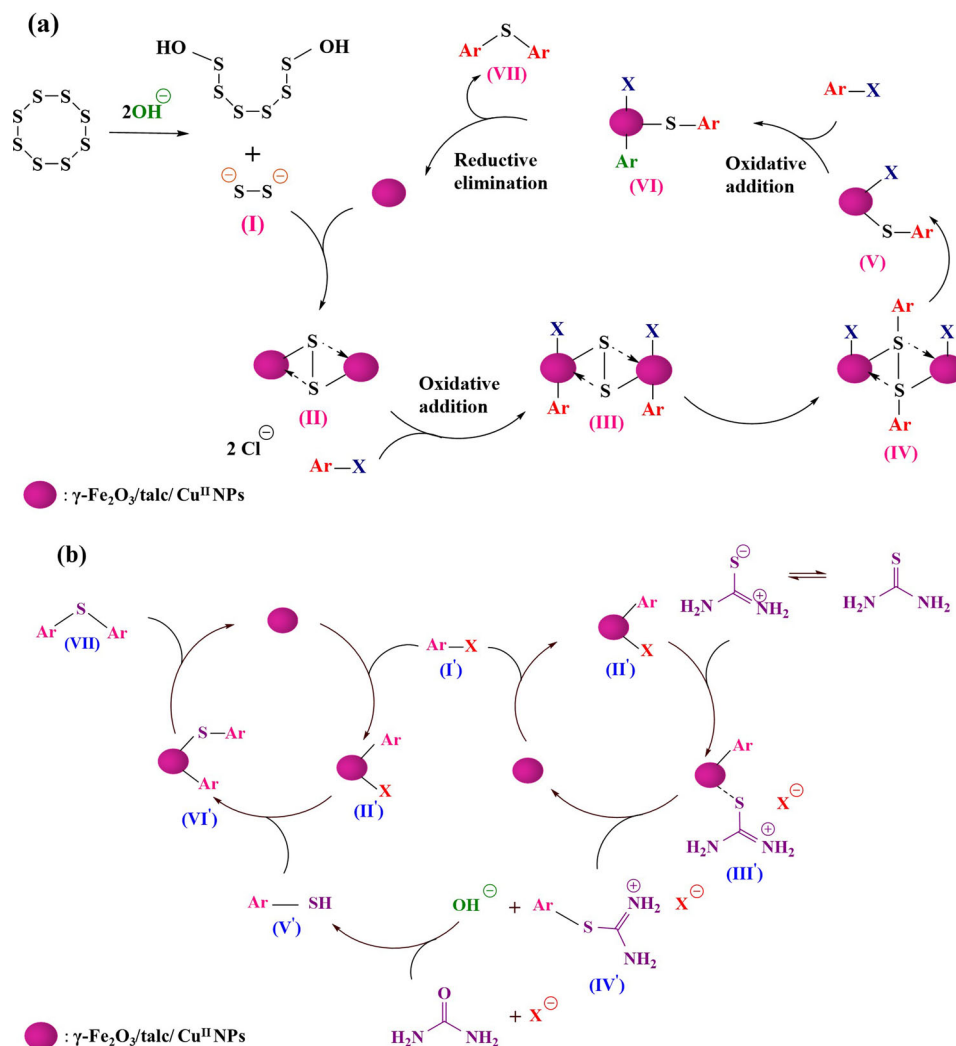
2.2.1. Catalyst reusability

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$_2$O$_3$/talc/Cu^{II} NPs in C–S cross-coupling reaction *via* the reaction of iodobenzene with S$_8$ or thiourea were investigated over five runs. The model reaction was performed under the optimized reaction conditions. Upon completion of the reaction (40/or 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 $100\,^\circ$C for 2 h and applied for a consecutive run under the same reaction conditions. The results (Figure S7, *see* "Supporting Information" file) showed that quantitative conversion/isolated yield of desired product was obtained for five runs. Loss of activity of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs was observed from the fifth run.

The structural stability of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs after five cycles in the reaction of iodobenzene with S$_8$ or 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$_2$O$_3$/talc/Cu^{II} NPs from the reaction of iodobenzene with S$_8$ or thiourea. (Figure S1(d and e), *see* "Supporting Information" file) Furthermore, XRD analysis of the 5th recovered catalyst demonstrated that the no changes were happened in the structure of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs during the C–S cross-coupling reaction of iodobenzene with S$_8$. (Figure S2c, *see* "Supporting Information" file) Additionally, the average crystalline size of the 5th recovered γ-Fe$_2$O$_3$/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 S4(c and d), (*see* "Supporting Information" file) no agglomeration was observed in the structure of 5th reused γ-Fe$_2$O$_3$/talc/Cu^{II} NPs. Also, the presence of Si, Mg, Fe, Cu and O elements in the composition of 5th reused γ-Fe$_2$O$_3$/talc/Cu^{II} NPs clearly authenticated the composition stability of this nanostructured catalyst (Figure S5b, *see* "Supporting Information" file). Based on ICP-OES analysis, the copper content of the fifth reused nanostructured catalyst from the reaction of iodobenzene with S$_8$ or thiourea is found to be 0.714/or 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$_2$O$_3$/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$_2$O$_3$/talc/Cu^{II} NPs in terms of functional groups, crystalline structure, morphology, particle size, and strong coordination of Cu^{II} ions to γ-Fe$_2$O$_3$/talc NPs even after five consecutive recycle runs.

Scheme 2. Recommended mechanism for the C–S cross-coupling reaction of aryl halides with S_8 (a) and thiourea (b) in the presence of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs.

2.2.2. 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 S_8 or thiourea was conducted under the optimized reaction condition. When approximately 50% (after 20/or 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/or 20 minutes without any catalyst under the same reaction conditions and monitored by TLC. (Figure S8, *see* "Supporting Information" file) It appeared that after 20/or 20 minutes in refluxing EtOH the reaction did not proceed further toward C–S cross-coupling reaction in the absence of γ-Fe$_2$O$_3$/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/or 0.07 mol%). It means that γ-Fe$_2$O$_3$/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.

2.2.3. Poisoning test

To further distinguish the true heterogeneity or homogeneity nature of catalyst, poisoning test was done under the optimized reaction conditions. For this purpose, in two separate flasks the reaction of iodobenzene with S_8 or thiourea was conducted in the presence and in the absence of ethylenediaminetetraacetic acid (EDTA) as an excellent scavenger of soluble Cu^{II} ions [120]. 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. (Figure S37) 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$_2$O$_3$/talc/Cu^{II} under the described reaction conditions (Figure S9).

In another variation, to show the unquestionable features of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs in C–S cross-coupling reaction of aryl halides with S_8 or thiourea, the efficiency of the present

Table 3. Comparison of the catalytic activity of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs with those of certain literature precedents using the C–S cross-coupling reaction of iodobenzene with S$_8$.

Entry	Catalyst	Mol%	Base	Solvent	Temperature (°C)	Time(min)	Reusability	Isolated yield (%)	Ref.
1	NiO(II)-GO	0.03 g	NaOEt	DMSO	120	30	5	97	[58]
2	Ni(II)-SBA-15	0.06 g	KOH	DMSO	120	1.40 (h)	5	96	[67]
3	Cu(II)-Vanillin-MCM-41	0.02 g	KOH	DMSO	110	45	5	90	[68]
4	SBA-16/GPTMS-TSC-Cu^{I}a	1.3	KOH	–	110	20	7	98	[56]
5	CuFe$_2$O$_4$ MNPs	25	Cs$_2$CO$_3$	PEG-400	120	20.5 (h)	6	97	[69]
6	CuI	10	LiOH·H$_2$O	DMF	100	36 (h)	–	100	[70]
7	Cu(OAc)$_2$	5	Cs$_2$CO$_3$	PEG-200	110	7 (h)	–	100	[66]
8	γ-Fe$_2$O$_3$/talc/Cu^{II}	1.1	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$_2$O$_3$/talc/Cu^{II}NPs with those of certain literature precedents using the C–S cross-coupling reaction of iodobenzene with thiourea.

Entry	Catalyst	Mol%	Base	Solvent	Temperature (°C)	Time (min)	Reusability	Isolated yield (%)	Ref.
1	Fe$_3$O$_4$@NiO/Co$_3$O$_4$	3.2:2.8*	KOH	PEG-400	100	20	8	95	[57]
2	NiO(II)-GO	0.03 g	NaOEt	DMSO	120	4 (h)	5	95	[58]
3	CuI-DMAPa	5	K$_2$CO$_3$	DMSO	120	10 (h)	–	80	[48]
4	Pd$_2$dba$_3$-Triphosb	2	Cs$_2$CO$_3$	1,4-dioxane	100	18 (h)	–	71	[49]
5	CuO NPs	5	Cs$_2$CO$_3$	DMSO	110	15 (h)	4	97	[50]
6	CuO@GO	0.01 g	Cs$_2$CO$_3$	DMSO	110	12 (h)	–	98	[51]
7	Cu(II)-2-MPEc @MCM-41	0.1 mmol	KOH	DMF:H$_2$O	130	12 (h)	6	85	[52]
8	Cu(OAc)$_2$.H$_2$O	5	K$_2$CO$_3$	DMSO	120	12 (h)	–	94	[53]
9	CuI	10	Cs$_2$CO$_3$	DMSO	120	24 (h)	–	63	[55]
10	SBA-16/GPTMS-TSCd – Cu^I	1.3	KOH	–	110	60	7	95	[56]
11	Magnetic nano CuFe$_2$O$_4$	10	K$_2$CO$_3$	DMF	120	12 (h)	6	94	[54]
12	γ-Fe$_2$O$_3$/talc/Cu^{II}	1.4	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. * The reported mol% of catalyst means the mol% ratio of Ni:Co in the catalyst.

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 Tables 3 and 4. As can be apparently seen from Tables 3 and 4 there is no doubt that all of the listed catalysts significantly improved the C–S cross-coupling reaction of aryl halides with S$_8$ or thiourea, nevertheless the reaction of iodobenzene with S$_8$ or thiourea in the presence of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs is much superior to almost all of the well-known catalyst systems in terms of the catalyst loading (Table 3, entries 4–7, Table 4, entries 1, 3–5 and 8–11), 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.

3. Material and methods

3.1. General

All chemical reagents and solvents were purchased from Merck Chemical Company and were used as received without further purification. The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel polygram STL G/UV 254 plates (using n-hexane: ethyl acetate = 9: 1 as eluent). The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The pH was determined by inoLab pH 7110 pH meter.The FT-IR spectra were recorded on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The NMR spectra were obtained on Brucker Avance 300 and 400 MHz instruments in CDCl$_3$ and DMSO-d_6. NMR spectra are calibrated using residual undeuterated solvent (TMS at 0.00 ppm ^{1}H NMR; CHCl$_3$ at 77.16 ppm ^{13}C NMR; DMSO-d_6 at 39.52 ppm ^{13}C NMR. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel%). The crystalline structure of the catalyst was analyzed by XRD using a D8 ADVANCE-Bruker diffractometer operated at 40 kV and 30 mA utilizing Cu Kα radiation ($\lambda = 0.154$ nm). Transmission electron microscopy (TEM) was performed with a Leo 912 AB microscope (Zeiss, Germany) with an accelerating voltage of 120 kV. FE-SEM images, EDX and EDX-mapping were recorded using a TESCAN, model: MIRA3 scanning electron microscope operating at an acceleration voltage of 30.0 kV and a resolution of about 200, 500 nm and 1 μm (manufactured in the Czech Republic). The magnetic properties of the catalyst were measured using a vibrating sample magnetometer (VSM, Magnetic Danesh Pajoh Inst.). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out with a Varian VISTA-PRO, CCD

(Australia). The talc was obtained from Gloria Interchem Pvt Ltd. India. Cu^{II} attached to magnetic natural talc (γ-Fe$_2$O$_3$/talc/Cu^{II} NPs) was prepared by the method reported previously [100]. All yields refer to isolated products after purification obtained by thin-layer chromatography on silica gel. Additional characterization data for the catalyst (Figures S1–S6) and products (Figures S11–S35) are presented in the Supplemental Materials.

3.2. 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 [113].

3.3. Typical procedure for preparation of diphenyl sulfide from the reaction of iodobenzene with S$_8$ or thiourea in the presence of γ-Fe$_2$O$_3$/talc/Cu^{II} NPs

γ-Fe$_2$O$_3$/talc/Cu^{II} NPs (1.1/or 1.4 mol%, 0.008/or 0.01 g) was added to a refluxing solution of iodobenzene (1.0 mmol, 0.203 g), S$_8$ or thiourea (0.5 mmol, 0.016 g/or 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/or 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 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 Na$_2$SO$_4$ 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%) or thiourea (0.182 g, 98%)).

4. Conclusion

In the present study, the application of the previously designed and characterized γ-Fe$_2$O$_3$/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$_8$ or 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$_8$ or 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$_2$O$_3$/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$_8$ or thiourea.

Disclosure statement

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