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Magnetically recoverable ferromagnetic 3D hierarchical core-shell Fe_3O_4@NiO/Co_3O_4 microspheres as an efficient and ligand-free catalyst for C−S bond formation in poly (ethylene glycol)

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ABSTRACT

A simple and efficient protocol for the synthesis of diaryl thioethers from the reaction of thiourea with a wide variety of aryl halides, including aryl iodides, aryl bromides and aryl chlorides in the presence of 3D hierarchical core-shell Fe_3O_4@NiO/Co_3O_4 microspheres has been described. This reaction enables the one-pot synthesis of diaryl thioethers in good to high yields using a non-toxic and magnetically separable catalyst in PEG-400 as an eco-friendly, safe, inexpensive and thermally stable solvent. Magnetic separation and reusability of catalyst for eight times without any significant loss of activity, the use of a commercially available, eco-friendly, cheap and chemically stable sulfur transfer agent and solvent, operational simplicity, environmentally benign, easier work-up procedure and cost efficiency make this method a promising candidate for potential applications in some organic reactions.

The catalytic activity of Fe_3O_4@NiO/Co_3O_4 as a novel and inexpensive catalyst was investigated in the C-S cross coupling reaction.
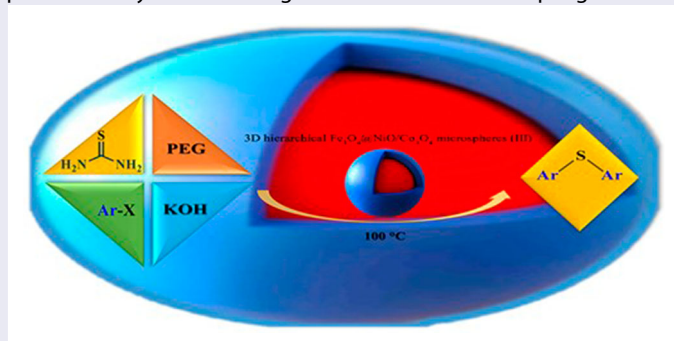
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1. Introduction

Today, among the carbon-heteroatom bond-forming reactions, carbon–sulfur bond formation is one of the significant organic transformations and powerful tools in making various arrangements of target compounds including pharmaceutical to biological molecules [1–4] and novel precurso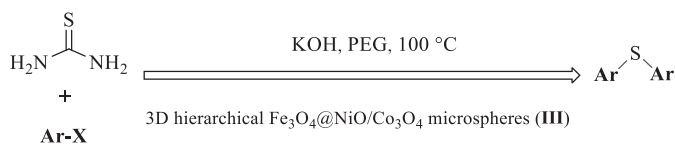rs in the material science as well [5,6]. Sulfur-containing organic molecules particularly, diaryl thioethers and their derivatives have been recognized in numerous drugs, which are used for the cure of some diseases such as Diabete, Alzheimer, cancer, Parkinson, HIV, and inflammatory and microbial diseases as well. [3,4,7,8] Even though, several methodologies have been designed for the C–S bond formation (including reaction of aryl diazoniumfluoroborate with diaryl disulfides [9], coupling of aryl or alkyl thiols with aryl halides [10,11], cross-coupling reaction of aryl halides and ethyl potassium xanthogenate [12], reaction of phenolic esters such as acetates, triflates, tosylates and phosphonates with alkyl halides by using thiourea as a sulfur source [13], reaction of aryl halides with aminothiourea [14], oxidative sulfidation of diaryl disulfides with aryltrimethoxysilanes [15], reduction of aryl sulfones or aryl sulfoxides [16,17] and reaction of thiourea with aryl halides [18–28]), most of them require drastic reaction conditions such as strong bases, elevated temperatures, strong reducing agents, direct use of volatile, hazardous, and foul-smelling thiols, toxic and expensive organic solvent, stoichiometric amounts of the catalyst as well as expensive ligands together with highly toxic metals. Furthermore, it should be noted that most of the previous methods using homogeneous catalysts (that cannot be separated and recovered simply), which represent more obstacles for the utility of this chemistry in parallel synthesis and in the industry. Today, with respect to the importance of green chemistry legislations, researches in this field of science should be moving further towards economical, efficient, beneficial and eco-friendly methods and cheap and safe resources for C–S bond generation.

Metal oxides which are involved in many petrochemicals, intermediates, fine and pharmaceutical chemicals were found to be one of the most important heterogeneous catalysis which catalyzed a wide variety of reactions [29,30]. Amongst them, NiO and Co_3O_4 have possessed increasing consideration due to their commercial and potential applications in various fields, including catalysis electrode materials, solid-state sensors and super capacitors [31].

Very recently, due to our interest towards the extension of environmentally friendly synthetic methods [19,32], the successfully synthesized 3D hierarchical core-shell $Fe_3O_4@NiO/Co_3O_4$ microspheres (Scheme 1) was efficiently used in the C-P cross-coupling reaction under mild conditions without using toxic solvent [31]. In the present study, based on our previous experience for the synthesis of diaryl thioethers [19], we sought to explore the synthesis of diaryl thioethers from the reaction of aryl halides with thiourea (as a solid, stable, cheap and odorless sulfur transfer agent) in the presence of 3D hierarchical core–shell $Fe_3O_4@NiO/Co_3O_4$ microspheres as a magnetically separable nanostructured heterogeneous catalyst in the absence of an inert atmosphere (Scheme 2).
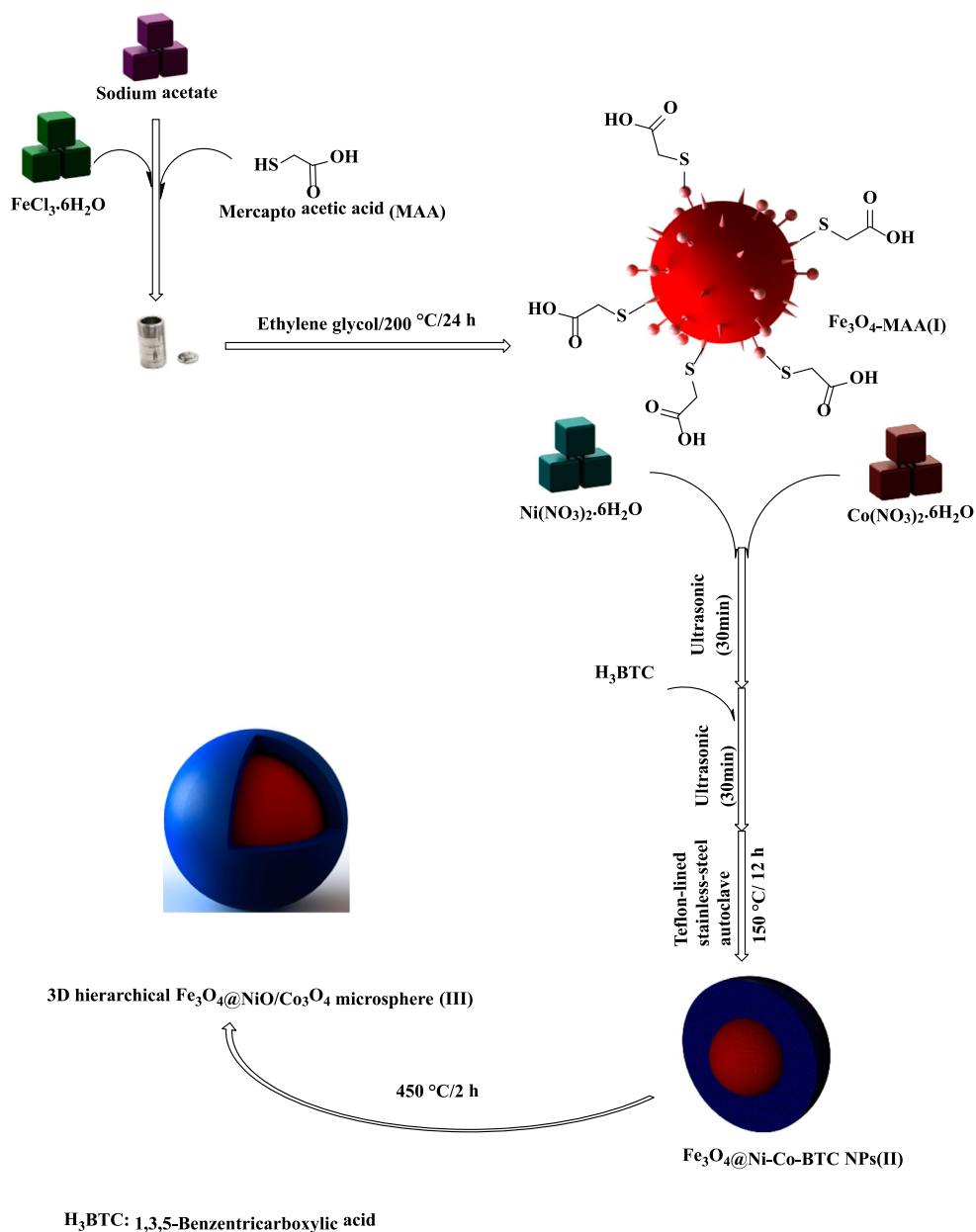
Scheme 1. The synthetic route for the preparation of 3D hierarchical core-shell $Fe_3O_4@NiO/Co_3O_4$ microspheres (III).

$$\underset{\substack{H_2N \overset{\displaystyle S}{\underset{\displaystyle +}{\bigparallel}} NH_2 \\ \textbf{Ar-X}}}{} \xrightarrow[\text{3D hierarchical Fe}_3O_4@NiO/Co_3O_4 \text{ microspheres (III)}]{\text{KOH, PEG, 100 °C}} Ar{\overset{\displaystyle S}{\diagup}}\!\diagdown Ar$$

X= I, Br, Cl

Ar = C_6H_5, 4-$H_3COC_6H_4$, 4-$H_3CC_6H_4$, 4-NCC_6H_4, 4-$O_2NC_6H_4$, 4-$H_2NC_6H_4$, 2-$H_2NC_6H_4$, 4-HOC_6H_4, 4-ClC_6H_4,

1-Naphthyl, 2-Thienyl, 2,4-$(O_2N)_2C_6H_3$.

Scheme 2. C–S coupling reaction in the presence of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres (**III**).

2. Results and discussion

To obtain the standard reaction conditions, at the first, a series of experiments were performed with variation of reaction parameters such as solvent, base, temperature and catalyst loading (Table 1). Initially, our studies began with the reaction between iodobenzene (1.0 mmol) and thiourea (0.5 mmol) in PEG-400 at 110°C under normal atmospheric conditions. Adjusting the reaction mixture in the absence of catalyst and base/or in the absence of catalyst /or in the absence of base showed that no product was formed even after a long reaction time (Table 1, entries1–3). The desired product was obtained in 95% yield using 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres and KOH (Table 1, entry 4). We then carried out our investigations to identify the best solvent for this reaction. Among the various solvents screened (PEG, DMF, DMSO, toluene, H_2O, THF, EtOH, and solvent free conditions), PEG-400, with negligible vapor pressure (as an inexpensive, thermally stable, recoverable, and non-toxic media for environmentally friendly and safe chemical reactions) was shown to be the best solvent for C–S coupling reaction in the presence of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres and this was then used as a standard for the optimization of other parameters (Table 1, entries 5–11) [33]. It was evident that the coupling product could be obtained in DMF, DMSO, and H_2O but in lower yield or after a prolonged reaction time, and a trace amount of product could be detected when the reaction was carried out in toluene, THF, EtOH and solvent free conditions. Because of the essential role of base in the C—S coupling reaction, different bases were tested for this transformation (Table 1, entries 12–15). According to the obtained results, KOH was specified to be the most efficient base in C—S coupling reaction in the presence of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres. It was further observed that 4 equivalents of KOH resulted in the best yield in 20 min at 110°C (Table 1, entries 16–18). Screening was also performed at different temperatures. (Table 1, entries 19–21) Ultimately, the ideal temperature for the reaction was found to be 100°C. Finally, the effect of catalyst loading on the yield and reaction rate was also examined (Table 1, entries 22–23). Obtained results revealed that the amount of catalyst influenced the outcome of C–S coupling reaction and the higher yield was attained in the presence of 0.01 g (3.2: 2.8 mol% ratio of Ni:Co) of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres. To probe more fully the role of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres in the C–S coupling reaction, a series of

Table 1. Synthesis of diphenyl sulfide from the reaction of iodobenzene with thiourea catalyzed by 3D hierarchical core-shell $Fe_3O_4@NiO/Co_3O_4$ microspheres under different reaction conditions.
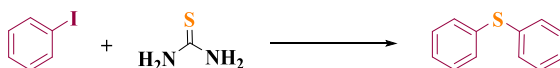
Entry	Catalyst (mol% ratio of Ni:Co)[a]	Molar ratio of iodoben-zene/base	Base	Solvent	Temperature (°C)	Time (h)	Isolated yield (%)
1	–	1/0	–	PEG-400	110	24	–
2	–	1/2	KOH	PEG-400	110	24	–
3	3.2: 2.8	1/0	–	PEG-400	110	24	–
4	3.2: 2.8	1/2	KOH	PEG-400	110	1	95
5	3.2: 2.8	1/2	KOH	DMF	110	3	60
6	3.2: 2.8	1/2	KOH	DMSO	110	4	95
7	3.2: 2.8	1/2	KOH	Toluene	Reflux	5	Trace
8	3.2: 2.8	1/2	KOH	H_2O	Reflux	5	95
9	3.2: 2.8	1/2	KOH	THF	Reflux	5	Trace
10	3.2: 2.8	1/2	KOH	EtOH	Reflux	5	Trace
11	3.2: 2.8	1/2	KOH	-	110	5	Trace
12	3.2: 2.8	1/2	K_3PO_4	PEG-400	110	1.5	95
13	3.2: 2.8	1/2	K_2CO_3	PEG-400	110	3	60
14	3.2: 2.8	1/2	$NaHCO_3$	PEG-400	110	2	20
15	3.2: 2.8	1/2	Li_2CO_3	PEG-400	110	45 (min)	20
16	3.2: 2.8	1/5	KOH	PEG-400	110	20 (min)	95
17	3.2: 2.8	1/4	KOH	PEG-400	110	20 (min)	95
18	3.2: 2.8	1/3	KOH	PEG-400	110	20 (min)	85
19	3.2: 2.8	1/4	KOH	PEG-400	120	20 (min)	95
20	**3.2: 2.8**	**1/4**	**KOH**	**PEG-400**	**100**	**20 (min)**	**95**
21	3.2: 2.8	1/4	KOH	PEG-400	90	20 (min)	80
22	4.4: 3.9	1/4	KOH	PEG-400	100	20 (min)	95
23	1.92: 1.68	1/4	KOH	PEG-400	100	20 (min)	85
24[b]	0.01 (g)	1/4	KOH	PEG-400	100	2.5	Trace
25[c]	3.2	1/4	KOH	PEG-400	100	1.5	60
26[d]	2.8	1/4	KOH	PEG-400	100	1.5	70

[a]The mol% result was obtained from ICP-OES analysis.
[b]Reaction was performed in the presence of $Fe_3O_4@MAA$ NPs.
[c]Reaction was performed in the presence of $Fe_3O_4@Co_3O_4$ NPs as catalyst.
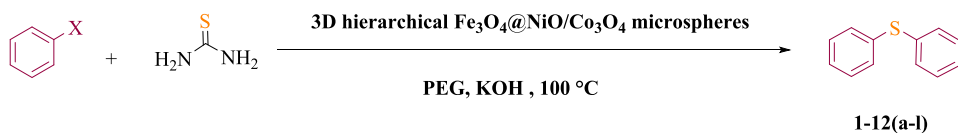[d]Reaction was performed in the presence of $Fe_3O_4@NiO$ NPs as catalyst.

controlled experiments in the presence of $Fe_3O_4@MAA$ NPs (I), $Fe_3O_4@Co_3O_4$ NPs and $Fe_3O_4@NiO$ NPs, were carried out (Table 1, entries 24-26). It can be seen that trace amount of desired product was produced after long reaction time using $Fe_3O_4@MAA$ NPs. Also, in the presence of $Fe_3O_4@Co_3O_4$ NPs and $Fe_3O_4@NiO$ NPs, the C–S coupling reaction was sluggish and gained lower yield of desired product. The results, therefore, suggests that 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres is essential to the success of the reaction.

Next, to explore the scope of the C–S coupling reaction *via* this modified procedure (Table 1, entry 20), the reaction of various aryl halides with thiourea (as a commercial available and economic affordable reagent for the synthesis of aryl sulfides) was studied. (Table 2) As summarized in Table 2, the electronic nature of substitution played a major role in governing the reactivity of the aryl halides. Generally, synthesis of aryl thioethers with electron-withdrawing groups requires shorter reaction time than electron-donating ones. (Table 2, entries 2–4 vs. entries 5–6, entry 8 vs. entry 9 and entries 13–14 vs. entries

15–16) Our results reveal that aryl chlorides were not as reactive as aryl bromides and aryl iodides. (Table 2, entries 1–2 and 7–8 vs. entries 12–13) In these cases, the observed yields are less and there was no improvement in the yields even after prolonged reaction time. As
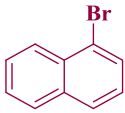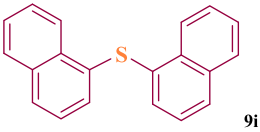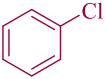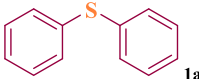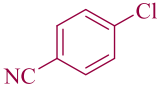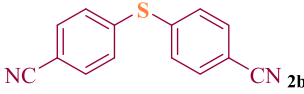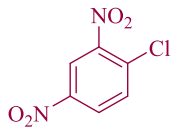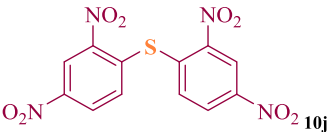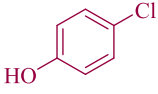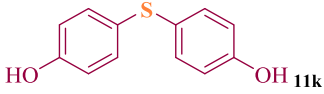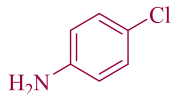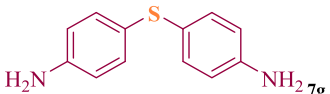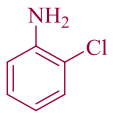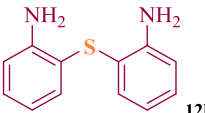
Table 2. Synthesis of diaryl sulfides from the coupling reaction of aryl halides with thiourea catalyzed by 3D hierarchical Fe$_3$O$_4$@NiO/Co$_3$O$_4$ microspheres.

Entry	Aryl halide	Product	Time (min)	Isolated yield (%)
1		1a	20	95
2		2b	20	95
3		3c	15	95
4		4d	80	45
5		5e	60	75
6		6f	80	70
7		1a	60	70
8		2b	60	80
9		7g	100	70
10		8h	4.5 (h)	75

(continued).

Table 2. Continued.

Entry	Aryl halide	Product	Time (min)	Isolated yield (%)
11		9i	6.5 (h)	65
12		1a	2.5 (h)	60
13		2b	2.5 (h)	65
14		10j	2.5/7 (h)	15/15
15		11k	3.5 (h)	55
16		7g	4 (h)	45
17		12l	24 (h)	Trace

can be seen, the reaction rate is sensitive to steric effects of the aryl halides. A sterically hindered *ortho*-substituted aryl halide proved to be problematic in the presence of 3D hierarchical core-shell $Fe_3O_4@NiO/Co_3O_4$ microspheres, and no cross-coupled product was detected even after 24 h (Table 2, entries 16–17). In the case of naphthyl and hetero-cyclic halides, the reaction time is high to obtain a reasonable yield of the corresponding symmetrical thioethers (Table 2, entries 10–11). To investigate the chemoselectivity of the present method, the reaction of 1-chloro-4-iodobenzene (as dihalogenated aryl halide) with thiourea was also tested which the iodide showed more reactivity (Table 2, entry 4). This fact was confirmed by the mass spectrometry (Figure 9, Supporting Information file).

In the present study, the progress of the reaction was monitored by disappearance of aryl halides and formation of C–S coupled product on TLC. All the prepared products were known compounds and isolated, purified and initially identified by mass spectrometry and comparison of their melting points with those reported previously or with authentic samples prepared by the conventional methods. Additionally, the structure of some selected products was further deduced from ^{1}HNMR and ^{13}CNMR spectral data. The spectral data of all products are given in 'Supporting Information' file.
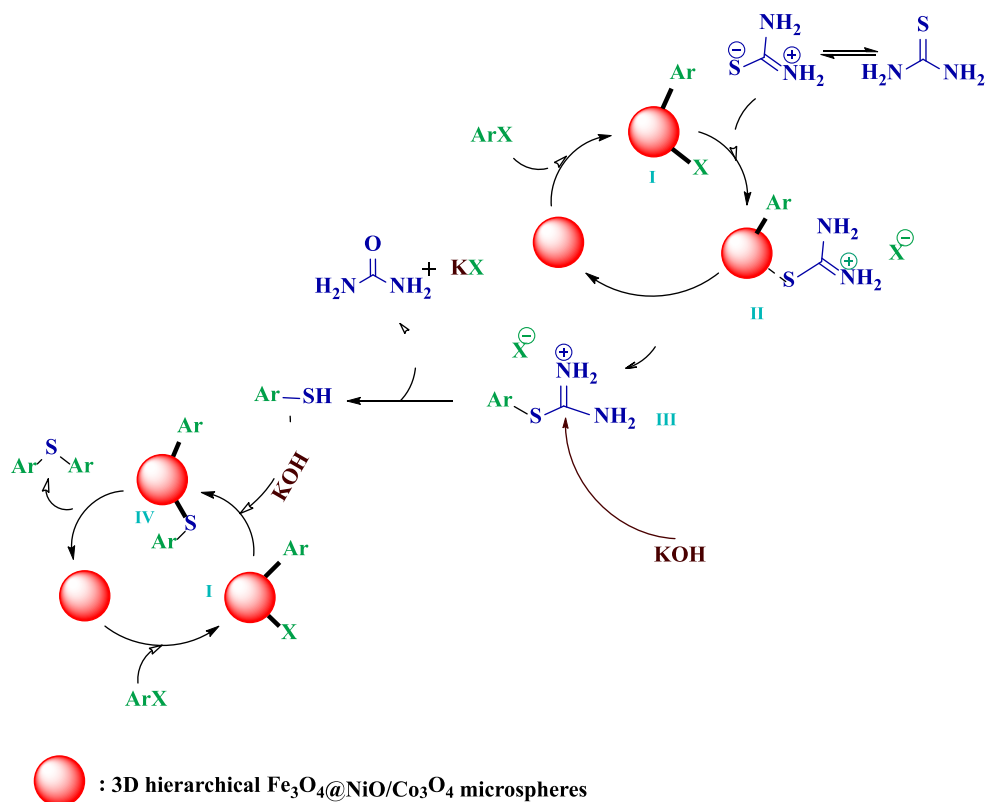
Scheme 3. Proposed mechanism for synthesis of diaryl thioethers by the reaction of aryl halides with thiourea in the presence of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres.

Based on the reported pathway in literature and also according to our previous experience [19,21], a proposed reaction mechanism for C–S coupling reaction of aryl halides with thiourea in the presence of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres is presented in Scheme 3. At the outset, through an oxidative addition reaction, the active sites of catalyst (Ni and Co) inserts into the C-X bond of aryl halide afforded intermediate (I). Subsequently, upon the reaction of thiourea with intermediate (I) followed by reductive elimination step, intermediate (II) and intermediate (III) were produced respectively along with the catalyst. In alkaline media, thiol moiety was generated smoothly and reacted with the intermediate (I) (which is produced in the oxidative addition step) to afford intermediate (IV). Finally, the desired C–S coupled product was obtained *via* a reductive elimination manner and the catalyst enters the next cycle. The results obtained from Table 1, entries 25–26, revealed that Ni and Co together in the MOF structure enhance the catalytic activity of 3D hierarchical $Fe_3O_4@NiO/Co_3O_4$ microspheres which accelerate the C–S coupling reaction.

Particularly, according to the green chemistry viewpoint, the separation of catalyst using an external magnetic field from the reaction mixture is a very convenient and efficient process in modern catalysis researches. Magnetic separation of the catalyst as an attractive alternative to filtration or centrifugation prevents loss of the catalyst and
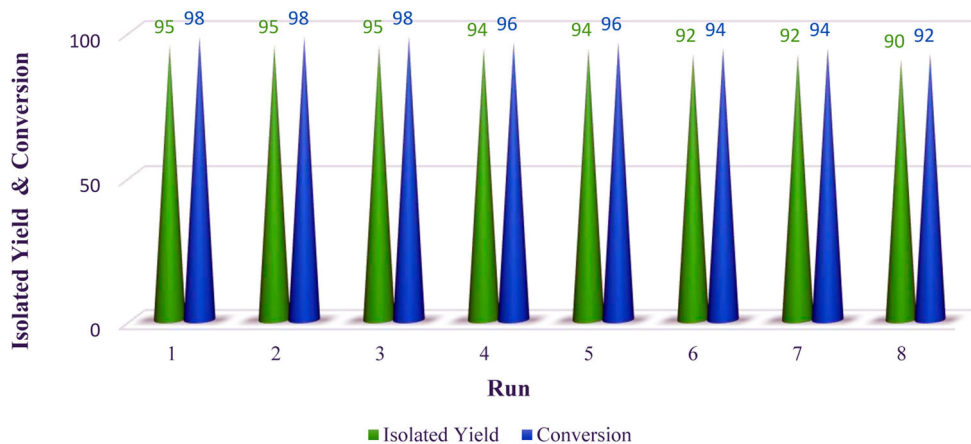
Figure 1. Reusability of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres in the C–S coupling reaction under the optimized reaction conditions.
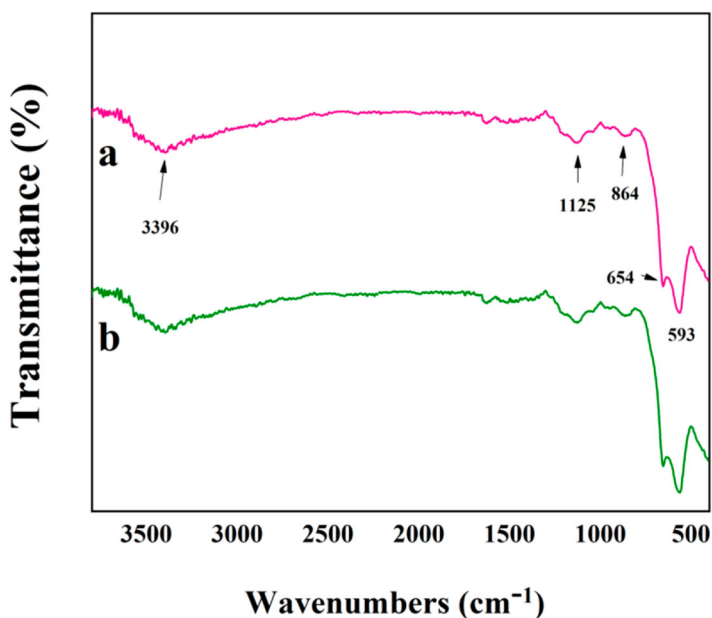
Figure 2. FT-IR spectra of (a) fresh 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres (b) and 8th reused 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres.

increases its reusability. Due to paramagnetic property, the magnetite Fe_3O_4 particles are amenable to magnetic separation. To demonstrate the consistency of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres in terms of activity and efficiency, the recovery and reusability of catalyst was studied in model reaction under the optimized reaction conditions. After the completion of the reaction, spent 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres was easily separated from the reaction mixture using an external magnetic field, followed by washing with EtOH (3 × 10 mL), and then dried at 70°C overnight for the

next run without considerable decrease of its catalytic activity. (Figure 1) As can be seen in Figure 1 no significant changes in yield of desired product were observed after regeneration until the 8th cycle.

Fourier transform infrared (FT-IR) spectroscopy was utilized to authenticate the structure of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres (**III**) and the 8th recovered nanocatalyst (Figure 2(a,b)). As it is evident from Figure 2(a), two characteristic absorption bands at 654 and 593 cm^{-1} were related to Co_3O_4, NiO and Fe_3O_4 stretching vibrations, respectively [32,34,35]. Furthermore, the stretching frequencies of hydroxyl groups on the surface of Fe_3O_4 NPs and asymmetric and symmetric stretching vibrations of Fe-O-H bond appeared as broad absorption bands at 3396, 1125 and 864 cm^{-1}, respectively [36], confirming the structure of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres (**III**). It is interesting to note that the shapes, positions, intensities and frequencies of the distinctive absorption bands are well preserved even after eight recycle runs, as can be seen in Figure 2(b). As well, the obtained ICP-OES results showed that the exact amount of metal ions (Co and Ni) are 3.2 and 3.2 mmol of cobalt as well as 2.8 and 2.7 mmol of nickel in 1.000 g of the fresh and the 8th reused 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres, respectively.

The catalytic efficiency of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres was compared with some selected previously reported catalysts in preparation of diaryl thioethers from the reaction of aryl halides with thiourea. (Table 3) It is evident from Table 3 that the reaction of iodobenzene with thiourea in the presence of 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres was completed more quickly than the other catalysts. More importantly, compared with other catalysts, 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres can be easily separated from the reaction mixture by means of a magnetic bar (Table 3, compare with entries 1–4, 6–8 and 10–11) and reused at least eight times without any significant loss of its catalytic activity as well (Table 3, entries 6, 7–8 and 11). Noticeably, using environmentally friendly solvent is another merit of this catalytic methodology (Table 3, entries 1, 4–8 and 10–11).

Table 3. Comparison of the catalytic activity of 3D hierarchical core-shell Fe_3O_4@NiO/Co_3O_4 microspheres with some literature precedents S-arylation reaction.

Entry	Catalyst	Solvent	Base	Temperature (°C)	Time (h)	Reusability	Yield (%)	Ref.
1	CuO nanoparticles	DMSO	Cs_2CO_3	110	15	4	98	[18]
2	SBA-16/GPTMS-TSC-CuI	–	KOH	110	1	7	95	[19]
3	CuI	PEG-200	Na_2CO_3	120	15	4	93	[20]
4	Cu(II)-2-MPE[a]@MCM-41	DMF/H_2O	KOH	130	12	6	85	[21]
5	Magnetic nano $CuFe_2O_4$	DMF	K_2CO_3	120	12	6	94	[22]
6	CuO@GO	DMSO	Cs_2CO_3	110	12	–	98	[23]
7	GO-N-isatin-Ni (II)	DMSO	NaOEt	120	4	–	95	[24]
8	MCM-41-2N-CuI	DMSO	Cs_2CO_3	120	24	–	65	[25]
9	mPANI/pFe_3O_4[b]	H_2O	KOH	Reflux	24	5	88	[26]
10	PdNP-PNF[c]	DMSO	KOH	130	2	4	95	[27]
11	Ni(II)-modified-SBA-15	DMSO	KOH	120	4	–	96	[28]
12	3D hierarchical core-shell Fe_3O_4@NiO/Co_3O_4 microspheres	PEG-400	KOH	100	20 (min)	8	95	Present study

[a] 2-methoxy-1-phenylethanone.
[b] mesoporous polyaniline/porous magnetic Fe_3O_4.
[c] Pd nanoparticles on the peptide nanofiber.

3. Conclusion

In summary, 3D hierarchical core–shell Fe_3O_4@NiO/Co_3O_4 microspheres was introduced as a magnetically separable nanostructured heterogeneous catalyst for the one-pot odorless preparation of diary thioethers from the reaction of aryl halides with thiourea. Experimental results illustrate that this hierarchical nanostructured catalyst could promote the C–S cross coupling reaction of a large library of functional substrates including electron-rich and electron-poor aryl iodides /or aryl bromides /or aryl chlorides with thiourea with a remarkable yield in a green solvent (PEG-400). The uniqueness and long-term durability of this catalyst can be related to its small nano crystalline size (10–47 nm, according to the XRD and TEM data), bimetallic core–shell nanostructure and using cobalt and nickel species as a low-cost, non-toxic and readily available metal ions in its structure. The notable features of the present study are as follows: (a) use of readily accessible and non-toxic sulfur transfer reagent, (b) short reaction times, (c) magnetic separation of the nanocatalyst by using an external, (d) low environmental impact and high recovery of the nanocatalyst at least for eight times without a significant decrease in its catalytic activity in the S-arylation reaction.

4. Experimental

4.1. Material and methods

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), sodium acetate (NaOAc), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), mercapto acetic acid (MMA), benzene-1,3,5-tricarboxylic acid (trimesic acid) (H_3BTC), ethylene glycol (99%) and absolute ethanol 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 thin layer chromatography on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) using KBr plates at room temperature in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. Mass spectra were recorded with a CH7A Varianmat Bremen instrument at 70 eV electron impact ionization, in m/z (rel.%). The NMR spectra were recorded on a Bruker Avance 400 MHz instrument in $CDCl_3$ and DMSO-d_6 as the solvents. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out on a 76004555 SPECTRO ARCOS ICP-OES analyzer. All yields refer to the isolated products after purification by thin layer chromatography.

4.2. Synthesis of Fe_3O_4-MAA NPs (I)

Fe_3O_4-MAA NPs (**I**) was synthesized through a simple solvothermal procedure [37]. Accordingly, $FeCl_3.6H_2O$ (4 mmol, 1.08 g), mercapto acetic acid (MAA) (0.6 mmol, 0.052 g) and sodium acetate (0.1 mol, 8.2 g) were orderly mixed together in 40 mL ethylene glycol at 60°C. The obtained yellow mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and kept at 200°C for 12 h to achieve Fe_3O_4-MAA NPs (**I**).

The precipitate was separated by magnetic decantation, washed with deionized water (3 × 20 mL), ethanol (3 × 20 mL) and dried at 70°C overnight.

4.3. Synthesis of Fe₃O₄@Ni-Co-BTC NPs (II)

To a suspension of 0.06 g Fe_3O_4-MAA NPs (**I**) in ethanol (20 mL) (dispersed in an ultra-sonic bath for 30 min), a solution of 1.7 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ (0.494 g) and 3.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ (1.017 g) in 20 mL ethanol was added. The obtained mixture was sonicated for 30 min. Then, 2.8 mmol of trimesic acid (0.588 g in 20 mL ethanol) was added to the resulting suspension and the obtained mixture was dispersed again for 30 min. The mixture was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 150°C for 12 h. As a final step, the obtained black product (Fe_3O_4@Ni-Co-BTC NPs (**II**)) was separated by magnetic decantation, washed with ethanol for three times and dried at 60°C [38].

4.4. Synthesis of 3D hierarchical Fe₃O₄@NiO/Co₃O₄ microspheres (III)

To achieve black powder 3D hierarchical Fe_3O_4@NiO/Co_3O_4 microspheres (**III**), the obtained Fe_3O_4@Ni-Co-BTC NPs (**II**) powder was put into an electrical furnace and annealed in air at 450°C for 2 h with a heating rate of 2°C min^{-1} [39].

4.5. Typical procedure for the preparation of diphenyl sulfide in the presence of 3D hierarchical core-shell Fe₃O₄@NiO/Co₃O₄ microspheres

To a stirred solution of iodobenzene (1.0 mmol, 0.204 g) and thiourea (0.5 mmol, 0.038 g) in PEG-400 (3.0 mL) at room temperature, 3D hierarchical core–shell Fe_3O_4@NiO/Co_3O_4 microspheres (3.2: 2.8 mol% ratio of Ni: Co, 0.01 g) and KOH (4 mmol, 0.224 g) was added. The resultant mixture was heated at 100°C for 20 min. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was allowed to cool, and diluted by a 1:1 mixture of ethyl acetate/water (6 mL). The catalyst was separated from the reaction mixture using an external magnetic field, followed by washing with EtOH (3 × 10 mL), and then dried at 70°C overnight for the next run. The combined organic extract was separated and dried with anhydrous Na_2SO_4. Afterwards, the solvent was completely removed under vacuum to give the crude product, which was purified by thin layer chromatography (ethyl acetate/ *n*-hexane, 1:5) to afford diphenyl sulfide in 95% yield (0.176 g).

4.5.1. Diphenyl sulfide [19] (1a)
Diphenyl sulfide (0.176 g, 95%); Colorless oil; ^{1}H NMR (400 MHz, CDCl₃): δ [ppm] = 7.34-7.31 (m, 5H), 7.29-7.25 (m, 3H), 7.23-7.19 (m, 2H); ^{13}C NMR (100 MHz, CDCl₃): δ [ppm] = 135.9, 131.2, 129.4, 127.2; MS (70 eV, EI); *m/z* (%): 186 (M$^+$, 12%), 184 (M-2, 100%), 108 (C_6H_4S, 90%), 76 (C_6H_4, 42%), 65 (C_5H_5, 40%), 51 (C_4H_3, 28%).

4.5.2. 4,4′-Thiodibenzonitrile [19] (2b)

4,4′-Thiodibenzonitrile (0.198 g, 84%); Yellow solid; mp 134–135 °C (Lit. 134–135 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.43 (d, J = 8.8 Hz, 4 H, Ar-H), 7.19 (d, J = 8.4 Hz, 4 H, Ar-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 140.6, 133.0, 131.2, 118.2, 111.4.

4.5.3. Bis (4-nitrophenyl) sulfane [19] (3c)

Bis (4-nitrophenyl) sulfane (0.231 g, 84%); Yellow solid; mp 149–150 °C (Lit. 149–150 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 7 δ 8.25 (dd, J = 8.4, 1.6 Hz, 4H), 7.64 (dd, J = 8.4, 2.0 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ [ppm] = 146.7, 142.2, 131.3, 124.8; MS (70 eV, EI), m/z (%): 276 (M$^+$, 20%), 275 (M-1, 40%), 123 (C$_6$H$_5$NO$_2$, 90%).

4.5.4. Bis (4-chlorophenyl) sulfane [40] (4d)

Bis (4-cholorophenyl) sulfane (0.123 g, 45%); white solid; mp 89–90 °C (Lit. 91–92 °C); MS (70 eV, EI), m/z (%): 254 (M$^+$,100%), 256 (M + 2,66%), 218 (C$_{12}$H$_8$ClS,20%), 184 (C$_{12}$H$_8$S, 82%), 143 (C$_6$H$_4$ClS,18%), 108 (C$_6$H$_4$S,28%).

4.5.5. Di-(p-tolyl) sulfane [19] (5e)

Di-(p-tolyl) sulfane (0.158 g, 74%); Colorless oil; (Lit. 43–46 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.23 (d, J = 8.4 Hz, 4 H, Ar-H), 7.10 (d, J = 7.6 Hz, 4H, ArH), 2.32 (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 137.1, 132.8, 131.2, 130.1, 21.3; MS (70 eV, EI), m/z (%): 212 (M-2, 50%), 91 (C$_7$H$_7$, 67%).

4.5.6. Bis (4-methoxyphenyl) sulfane [19] (6f)

Bis (4-methoxyphenyl) sulfane (0.172 g, 70%); Yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.27 (d, J = 8.8 Hz, 4 H, Ar-H), 6.83 (d, J = 8.8 Hz, 4 H, Ar-H), 3.78 (s, 6 H, OCH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 159.1, 132.9, 127.6, 114.9, 55.5; MS (70 eV, EI), m/z (%): 246 (M$^+$, 5%), 243 (M-2, 65%), 77 (C$_6$H$_5$, 80).

4.5.7. 4,4′-Thiodianiline [19] (7g)

4,4′-Thiodianiline (0.177 g, 82%); Brown solid; mp 107–108 °C (Lit. 107–108 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.15 (d, J = 8.0 Hz, 4 H, Ar-H), 6.60 (d, J = 8.0 Hz, 4 H, Ar-H), 3.67 (s, 4 H, NH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 145.8, 132.9, 125.2, 115.9.

4.5.8. Di (thiophen-2-yl) sulfane [19] (8h)

Di (thiophen-2-yl) sulfane (0.146 g, 74%); Yellow liquid; 1H NMR (400 MHz, CDCl3): δ [ppm] = 7.63–7.53 (m, 2H), 7.45–7.34 (m, 2H), 7.27–7.11 (m, 2H); 13C NMR (100 MHz, CDCl$_3$): δ [ppm] = 135.5, 132.7, 129.6, 137.47.

4.5.9. Di (naphthalen-1-yl) sulfane [27] (9i)

Di (naphthalen-1-yl) sulfane (0.214 g, 75%); White solid; mp 156–157 °C (Lit. 156–158 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ [ppm] = 8.43–8.40 (m, 2 H, Ar-H), 7.89–7.87 (m, 2 H, Ar-H), 7.78–7.76 (m, 2 H, Ar-H), 7.55–7.51 (m, 4 H, Ar-H), 7.32–7.30 (m, 4 H, Ar-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 134.3, 132.8, 132.6, 130.1, 128.8, 128.2, 126.9, 126.6, 126.0, 125.3; MS (70 eV, EI), m/z (%): 286 (M$^+$, 8%), 285 (M-1, 52%), 282 (M-4, 90%), 127 (C$_{10}$H$_7$, 60%).

4.5.10. 4,4′-Thiodiphenol [19] (11k)

4,4′-Thiodiphenol (0.137 g, 63%); White solid; mp 151–153 °C (Lit. 150–153 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 9.62 (s, 2H), 7.14 (d, J = 8.4 Hz, 4H), 6.73 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ [ppm] = 157.0, 132.7, 124.7, 116.3.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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