



Short communication

Nano cobalt ferrite catalyzed coupling reaction of nitroarene and alkyl halide: An odorless and ligand-free rout to unsymmetrical thioether synthesis



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ABSTRACT

This study describes an odorless protocol for the synthesis of unsymmetrical sulfides via cobalt ferrite (CoFe₂O₄) catalyzed cross-coupling reaction of nitroarenes with alkyl halides in the presence of thiourea as sulfur source under ligand-free conditions. The catalyst was recycled using external magnetic field and reused for ten consecutive runs in the reaction of nitrobenzene, thiourea and benzyl bromide without significant loss of activity. Apart from being magnetically separable, being inexpensive and air-stable are another important features of this catalytic system. All the products were formed in good yields and short reaction times.

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1. Introduction

Carbon-hetero atom bond formation is an important transformation in organic synthesis [1–4]. Among them, C–S bond formation due to vast application of aryl sulfide motives in pharmaceutical and biological active compounds such as antidiabetes, anti-inflammatory, anti-Alzheimer, anti-Parkinson, anticancer and anti-HIV formulations have been attracted a great attention [5,6]. Another interesting aspect of sulfide containing compounds is the ability to oxidize to sulfoxide and sulfone which are also vital building blocks in the structure of some medicine such as modafinil, sulindac, and esomeprazole [7,8]. The first obstacle faced with during C–S bond formation is disulfide bond formation as by-product which lead to get low yield of desired product [9]. On the other hand, the inherent tendency of sulfur to bind to transition metal makes the metal catalyst poisoned and ineffective and by deactivation of catalyst the reaction cannot proceed anymore [10]. There are many synthetic methods for C–S bond formation employing different coupling partners and different sulfur surrogates [11] such as thiourea [12], carbon disulfide [13], S₈ [14], metal sulfides [15], thioacetate [16] and sodium thiosulfate [17–22]. Li introduced thiols as S-source in diaryl sulfides formation by couplings of aryl halides with aryl thiols [23]. However, the use of volatile, foul smelling and expensive thiols is the main drawback of this method. Hajipour et al. reported palladium catalyzed thioetherification of aryl halide with potassium thiocyanate

which is limited to symmetrical diaryl thioethers formation [24]. To compete with these methods involving foul-smelling thiols as S-source, expensive metals such as palladium and environmentally pollutant aryl halides, studies on finding a protocol employing new coupling partner and inexpensive metal as catalyst have been paid a great attention. Rostami et al. used nitro arenes and alkyl halides as coupling partners in presence of Na₂S₂O₃·5H₂O at 120 °C to form unsymmetrical thioethers [25]. The main disadvantage of this method is using homogeneous catalytic system that leads to contamination of products to transition metal that is not favorable from synthetic point of view specially in medicinal synthesis. In order to minimize catalyst cost and catalyst contamination of the product using Co heterogenous catalyst are good strategies. Furthermore, Co is abundant, inexpensive and a variety of their salts are commercially available. On the other hand, heterogeneous catalysts can be easily separated from reaction mixture. In comparison to non-magnetic heterogeneous catalysts magnetic nano ones are in higher demand. The first important point to mention is reduction of catalytic activity during the separation and recovery from reaction mixture via filtration. Spinel ferrites as an important class of magnetic materials are good candidates as catalysts in organic transformations [26,27]. The other significant aspect to point out is the synergetic catalytic effect between metals used in ferrites which makes them efficient in organic transformations without any functionalization [28,29]. As a part of our continuing interest in the development of magnetic nanoparticles for organic reactions [30–31], we describe herein the development of magnetic nanoparticles of ferrite complex oxide catalysts for the odorless protocol of unsymmetrical thioether synthesis using

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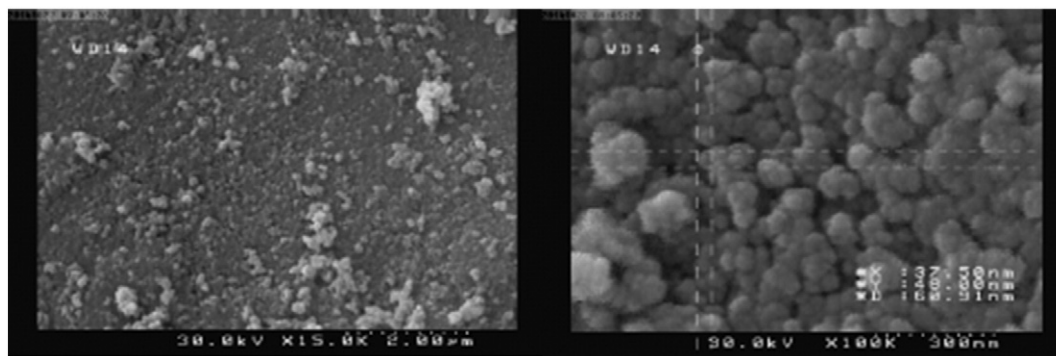


Fig. 1. SEM image of CoFe_2O_4 nanoparticles.

nitroarene as a user-friendly coupling partner and alkyl halide in the presence of thiourea as the source of sulfur.

2. Experimental

2.1. General data

All materials used are commercially available and were purchased from Merck and used without any additional purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker (Avance DRX-500) spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as solvent at room temperature. Chemical shifts δ were reported in ppm relative to tetramethylsilane as an internal standard. FTIR spectra of samples were taken using an ABB Bomem MB-100 FTIR spectrophotometer. The morphology of the catalyst was observed using a Philips XL30 scanning electron microscope (SEM). MS was recorded on Finnegan MAT 1020 mass spectrometer operating at 70 eV. Magnetic measurements were performed with an alternating gradient force (AGFM) G-856 magnetometer at RT. The X-ray fluorescence analysis was performed with a SPECTRO XEPOS spectrometer. The samples were characterized through crystallographic phase identification performed with a STADI P diffractometer using $\text{CuK}\alpha$ radiation and equipped with a graphite monochromator in the diffracted beam and an oscillation counter.

2.2. Synthesis of CoFe_2O_4

The solutions of iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (100 mL, 0.2 M) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (100 mL, 0.1 M) were prepared separately and mixed together. After stirring for an hour, a solution of NaOH (~15 mL, 3 M) was added slowly (during 30 min) to the flask in order for pH to reach 12. Finally, oleic acid (3 drops) was added to the solution as surfactant to prevent the aggregation and agglomeration of the nanoparticles. Then, the suspension was vigorously stirred using a magnetic stirring bar at 90°C for 2 h. After complete precipitation, the residue was washed with double distilled water (3×25 mL) and dried in an oven at 90°C over night; then it was calcinated at 600°C for 5 h. The final product is a black powder showing magnetic properties.

2.3. General procedure for the synthesis of unsymmetrical sulfides

A glass tube was charged with nitroarene (1 mmol), alkyl halide (1.2 mmol), thiourea (1.3 mmol), KOAc (1.5 mmol), DMSO (1 mL) and CoFe_2O_4 (5 mol%). The reaction mixture was stirred at 80°C for an appropriate amount of time. The progress of the reaction was monitored using TLC (*n*-hexane– EtOAc , 9:1). After completion of the reaction, the reaction mixture was allowed to cool to room temperature.

Table 1
Optimization of reaction conditions for C–S bond formation.^a

Entry	Base	Solvent	S-source	Temperature ($^\circ\text{C}$)	Yield (%) ^b
1	KOH	PEG(600): H_2O	Thiourea	80	30
2	K_2CO_3	PEG(600): H_2O	Thiourea	80	15
3	KOAc	PEG(600): H_2O	Thiourea	80	80
4	KOtBu	PEG(600): H_2O	Thiourea	80	50
5	Cs_2CO_3	PEG(600): H_2O	Thiourea	80	38
6	Et_3N	PEG(600): H_2O	Thiourea	80	77
7	KOAc	1,4 Dioxane	Thiourea	80	25
8	KOAc	Toluene	Thiourea	80	20
9	KOAc	H_2O	Thiourea	80	NR
10	KOAc	DMSO	Thiourea	80	88
11	KOAc	Ethanol	Thiourea	80	10
12	KOAc	DCE	Thiourea	80	9
13	KOAc	DMF	Thiourea	80	78
14	KOAc	CH_3CN	Thiourea	80	32
15	KOAc	DMSO	KSCN	80	NR
16	KOAc	DMSO	$\text{Na}_2\text{S}_2\text{O}_3$	80	NR
17	KOAc	DMSO	Thiourea	100	89
18	KOAc	DMSO	Thiourea	50	10
19	KOAc	DMSO	Thiourea	RT	trace

^a Reaction conditions: nitrobenzene (1 mmol), benzyl bromide (1.2 mmol), base (1.5 mmol), S-source (1.3 mmol), solvent (1 mL), catalyst (5 mol%), 90 min.

^b Isolated yield.

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