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Magnetically recyclable iron oxide-supported copper oxide nanocatalyst (Fe_3O_4–CuO) for one-pot synthesis of *S*-aryl dithiocarbamates under solvent-free conditions

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A green, convenient and efficient procedure is reported for the synthesis of *S*-aryl dithiocarbamates by a simple one-pot three component Ullmann-type condensation of an amine, carbon disulfide and an aryl iodide. Magnetically separable and reusable copper oxide (Fe_3O_4-CuO) nanoparticles is used as a heterogeneous catalyst under base- and solvent-free conditions. Nanoparticles with average size of 10-20 nm has been successfully prepared by a simple precipitation method in aqueous medium from readily available inexpensive starting materials. The catalyst could be easily separated from the reaction mixture by using an external magnet and recycled four times without significant loss in its activity.

Introduction

Supported-heterogeneous catalysts have received a paramount attention in recent years and are an integral part of catalysis science and technology. Due to easy separation and purification process of these catalytic systems, most important organic chemistry industries rely on them.[1-5] Consequently, it is important to design unique supported-heterogeneous catalytic systems for organic transformation; the most recent efforts being the synthesis of metal or metal oxides supported catalysts or nanocatalysts.[6-9]

Several inorganic materials such as silica, carbon, alumina, zirconia and iron oxides, as well as organic polymers, have been used as a catalyst support for metal and metal oxide nanoparticles;[10-16] among them, inexpensive iron oxides have gained much attention due to their unique characteristics such as high surface area and anchoring possibilities for immobilization of active nanocatalysts. They have been well investigated as environmentally benign catalysts or support in various important organic transformations.[17-23] Furthermore, their magnetic response, as an alternative to filtration, provide an efficient separation and recovery strategy and prevents loss of catalyst and increases the reusability.[24-26]

Copper-catalyzed heteroatom cross-coupling reactions (C–N, C–O and C–S) are very powerful tools in modern organic synthesis. They provide a uniquely easy and convenient accessibility to a wide range of structural variations.[27-34] Particularly, C–S bond forming reactions attracted significant interest because of the frequent occurrence of these structural units in biologically active molecules.[35-41]

The main disadvantage of using neat metal and metal oxide nanoparticles as catalyst is their poor recyclability and leaching effects finally leading to decreased yields. To overcome this problem, copper and copper oxide supported catalysts and nanocatalysts are employed in various organic reactions. Selected recent examples include an impregnated copper on magnetite in the synthesis of propargylamine[42] and 1,3-diynes,[43] iron oxide-supported copper oxide nanoparticles for the synthesis of pyrazole derivatives, 4-methoxyaniline and Ullmann-type condensation reactions[44] and lepidocrocite supported copper oxide nanocatalyst (Fe-CuO) for the synthesis of imidazole.[45]

Organic dithiocarbamates have received much attention because of their interesting chemistry and wide range of utilities. They have many potential applications as versatile synthetic intermediates,[46-52] linkers in solid phase organic synthesis,[53,54] protecting groups in peptide synthesis,[55,56] agrochemicals,[57-59] and biologically active compounds.[60,61] They are used in the rubber industry as vulcanization accelerators,[62,63] in medicinal chemistry[64-67] and recently as single precursor sources for the preparation of nanoparticles.[68-71] Conventional methods for their synthesis involve reactions of amines with toxic and expensive reagents, such as thiophosgene or an isothiocyanate, which are not environmentally acceptable.[72-74]

Recently, several one-pot procedures reacting amines with carbon disulfide and alkyl/aryl halides, α,β-unsaturated compounds or epoxides in water, in absence or presence of metals have been developed to produce simple alkyl and aryl dithiocarbamates.[75-80] However, only a few methods are available to access *S*-aryl and *S*-vinyl dithiocarbamates. Some of the procedures are involved with the Wittig reaction of aldehydes with phosphonium ylides[81] or reaction of the sodium salt of dithiocarbamic acid with hypervalent iodine compounds.[82-84] Clearly, simple methods for the synthesis of *S*-aryl and *S*-vinyl dithiocarbamates would be highly desirable.

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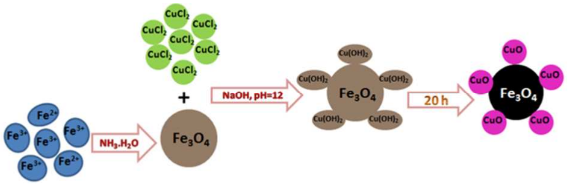
Recently, a new protocol based on the Ullmann-type coupling of sodium dithiocarbamates with aryl iodides and vinyl bromides catalyzed by CuI in the presence of a ligand, N,N-dimethylglycine, in DMF has been reported by Liu and Bao.[85] Moreover, Ranu et al. reported a one-pot three-component condensation of aryl/styrenyl halides, carbon disulfide, and amines using copper nanoparticles for the synthesis of aryl and styrenyl dithiocarbamates in water.[86] They also reported a catalyst-free procedure for the synthesis of *S*-aryl dithiocarbamates using aryldiazonium fluoroborate in water at room temperature.[87]

In our previous work, we reported regioselective metal- and solvent-free synthesis of *S*-vinyl dithiocarbamates.[88] Herein, a novel, convenient and efficient procedure is reported for the one-pot synthesis of *S*-aryl dithiocarbamates by Ullmann-type condensation of an amine, carbon disulfide and an aryl iodide using magnetically separable and reusable copper oxide nanoparticles (Fe_3O_4-CuO MNPs.) under base- and solvent-free conditions.

Results and discussion

The Fe_3O_4-CuO MNPs. were prepared following the literature [44, 89] (Scheme 1). The structure of nanocatalyst was established previously [11, 44, 89], in present work it was also characterized by X-ray diffraction (XRD), inductive coupled plasma optical emission spectroscopy (ICP-OES) and transmission electron microscopy (TEM).



Scheme 1. Synthesis of Fe_3O_4-CuO nanocatalyst.

Based on the ICP-OES analysis, the weight percentage of Cu was determined to be 4.50 %. The phase structure and crystallinity of Fe_3O_4 and Fe_3O_4-CuO nanoparticles were investigated by XRD, and the results are given in Fig. 1. For the XRD pattern of Fe_3O_4 nanoparticles (curve a), the diffraction peaks at $2\Theta = 29.4°, 35.8°, 44.7°, 54.8°, 58.8°, 65.7°$ matched well with the (220), (311), (400), (422), (511), (440) planes of Fe_3O_4 (JCPDS 79-0419). Besides typical peaks of Fe_3O_4, four new peaks with 2Θ values of 31.8°, 39.4°, 51.5° and 61.1° were indentified in the XRD pattern of Fe_3O_4-CuO (curve b), and they were indexed for the crystal faces of (110), (111), (020), (311) of monoclinic phase of CuO crystals (JCPDS 048-1548). The crystallite size of Fe_3O_4 nanoparticles, calculated using the Debye-Scherrer equation, from the $2\Theta=35.8°$ peak, was found to be 13 nm and the crystallite size of CuO nanoparticles, from the $2\Theta=39.4°$ peak, was found to be 17 nm.

The TEM image of Fe_3O_4-CuO (Figure 2) shows uniform-sized magnetic nanoparticles with somewhat spherical morphology. The average size of Fe_3O_4-CuO was in the range of 10-20 nm.

After the successful preparation and characterization of Fe_3O_4-CuO, its catalytic activity was examined for one-pot synthesis of *S*-aryl dithiocarbamates. For optimization of the reaction conditions, such as solvent, reaction time and reaction temperature, the model reaction of phenyl iodide, pyrrolidine and carbon disulfide has been selected. The results are summarized in Table 1.

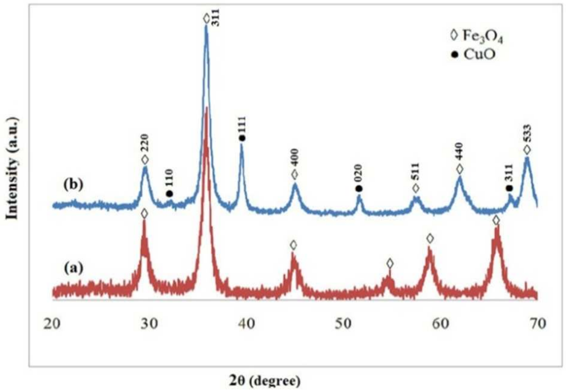


Figure 1. XRD patterns of (a) Fe_3O_4 MNPs and (b) Fe_3O_4-CuO MNPs.

It should be noted that no product formation was observed in the absence of Fe_3O_4-CuO nanoparticles at room temperature. The same reaction was repeated at 130 °C, and only a trace amount of coupling product was formed (Table1, entry 16). The reaction yield when catalytic amount of Fe_3O_4-CuO MNPs. were added in solvent-free condition at 90 °C, after 10 h, was 70% (Table 1, entry 10), while at 130 °C after 8 h the yield was 96% (Table 1, entry 11). Bases such as K_2CO_3 and KOH are found to have no significant effect in the yield of the reactions (Table 1, entries 1-8). The results showed that 130 °C was required for the coupling reaction to give 96% yield of the product (Table 1, entry 11). Shorter or longer reaction time than 8 h and lower or higher temperature than 130 °C decelerated the reaction rate and led to lower product yields (Table 1, entries 9-15). Commercial available $CuFe_2O_4$ also used as catalyst in the model reaction and gave lower yield (Table 1, entry 17).

With optimized reaction conditions in hand, other *S*-aryl dithiocarbamates were prepared by the coupling reaction of several substituted aryl iodides with dithiocarbamate anions, generated *in situ* by the reaction of carbon disulfide and amines (Scheme 2). The results are summarized in Table 2. A variety of electron-donating and electron-withdrawing substituents in the aromatic ring, such as OMe, CH_3, Cl and COMe, are compatible in this reaction. Unfortunately, bromobenzene gave only trace amounts of desired product under the conditions described (Table 2, entry 17). Ranu et al., used Cu nanoparticles as a catalyst for the synthesis of *S*-aryl dithiocarbamates with the similar substrates.[86] But the present

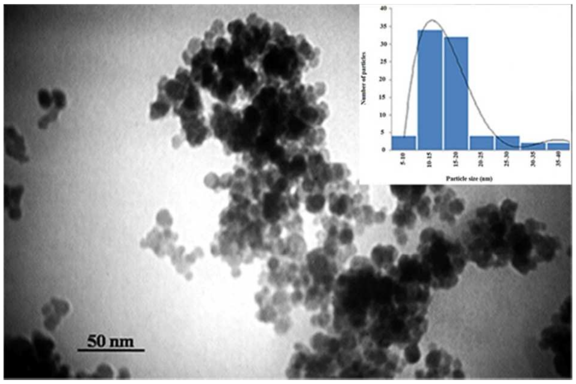
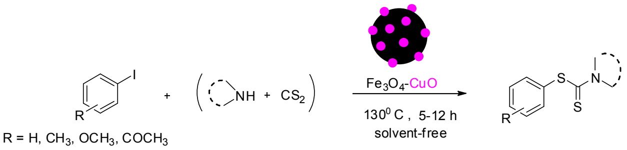


Figure 2. TEM image of Fe_3O_4-CuO MNPs showing particle size distribution: the corresponding histogram is superimposed onto image.

catalytic system is separable and can be recycled and used four times without significant loss in its catalytic activity. The present procedure provides a one-pot approach and avoids the use of sodium salt of dithiocarbamic acid that Bao et al., used for the synthesis of *S*-aryl dithiocarbamates.[85] In addition, present protocol did not require a base or a ligand and avoids the use of toxic organic solvents by performing solvent-free conditions.



Scheme 2. Coupling reaction of various aryl iodides with dithiocarbamates catalyzed by Fe_3O_4-CuO MNPs.

The stability of Fe_3O_4-CuO nanocatalyst and its activity were investigated by recycling experiments for the reaction between pyrrolidine, CS_2 and phenyl iodide under the optimized conditions reported in Table 1 (entry 11). After each cycle, the catalyst was separated by an external magnet, washed with ethanol, dried at 60 °C in a vacuum oven to remove residual solvents, and used for the next cycle. It was found that Fe_3O_4-CuO nanoparticles could be recycled four times without significant loss of its initial catalytic activity. The reusability test has been shown in Table 3.

In order to prove that the Fe_3O_4-CuO nanocatilyst is heterogeneous, a standard leaching experiment was conducted by the hot filtration method. The coupling reaction of phenyl iodide, pyrrolidine and carbon disulfide proceeded for 30 min in the presence of Fe_3O_4-CuO nanocatilyst at 130 $^{\circ}$C, then the catalyst was removed using an external magnet. It was observed that the reaction did not reach completion even after 24 h. This clearly confirmed that no homogeneous catalyst was involved. ICP-OES analysis of the filtrate (hot) was also done to determine the leaching of metal in the reaction mixture and revealed the absence of Fe and Cu species in the filtrate.

Experimental Section

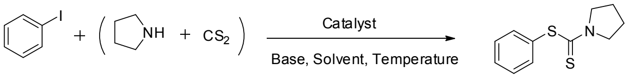
Materials and Reagents

The reagents such as $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $CuCl_2.2H_2O$, phenyl iodide, CS_2 and amines were purchased from Sigma-Aldrich and Merck and were used as received without any further purification.

Measurements

The ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ using TMS as an internal standard. Thin layer chromatography (TLC) was carried out on Merck 60 GF 254 plates coated with a 0.2 mm layer of silica gel. The spots were visualized using UV 254 light. The Fourier transformation infrared (FT-IR) spectra were recorded (Shimadzu, Japan) as KBr pellets in the wavenumber range 4000-400 cm^{-1}. Transmission electron microscopy (TEM) images were obtained on an EM10C (Zeiss) transmission electron microscope at an accelerating voltage of 80 kV. Powder X-ray diffraction (XRD) measurements were collected using Philips PW3710 diffractometer (Co Kα radiation (λ□= 1.78Å)). Copper elemental analysis was determined with an inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo Scientific, IRIS Intrepid II, USA) coupled to a

Table 1. Optimization of the reaction conditions for coupling reaction of phenyl iodide with dithiocarbamate anion.



Entry	Catalyst	Solvent	Base	Time (h)	Temp (°C)	Yield ^{a,b} (%)
1	Fe_3O_4-CuO	DMF	K_2CO_3	8	70	60
2	Fe_3O_4-CuO	DMSO	K_2CO_3	5	80	65
3	Fe_3O_4-CuO	Toluene	K_2CO_3	10	80	57
4	Fe_3O_4-CuO	H_2O	K_2CO_3	10	90	40
5	Fe_3O_4-CuO	DMF	KOH	8	70	50
6	Fe_3O_4-CuO	DMSO	KOH	5	80	58
7	Fe_3O_4-CuO	Toluene	KOH	10	80	45
8	Fe_3O_4-CuO	H_2O	KOH	10	90	35
9	Fe_3O_4-CuO	-	-	5	90	60
10	Fe_3O_4-CuO	-	-	10	90	70
11	Fe_3O_4-CuO	-	-	8	130	96
12	Fe_3O_4-CuO	-	-	8	150	90
13	Fe_3O_4-CuO	-	-	10	130	96
14	Fe_3O_4-CuO	-	-	5	130	80
15	Fe_3O_4-CuO	-	-	3	130	70
16	-	-	-	8	130	Trace
17	$CuFe_2O_4$			8	130	85

[a] Isolated yield.

[b] Reaction condition: Catalyst (20 mg), Phenyl iodide (1 mmol), Pyrrolidine (1.2 mmol), CS_2 (3 mmol), Base (1.5 mmol) in 3 mL of solvent. NR= no reaction

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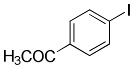
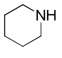
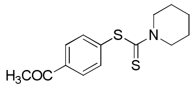
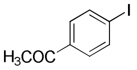
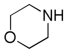
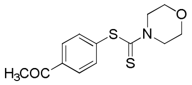
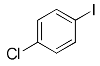
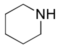
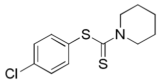
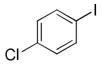
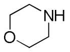
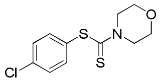
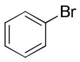
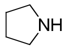
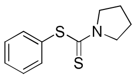
Table 2. Fe_3O_4-CuO MNPs. Catalyzed coupling of aryl iodides with dithiocarbamates.

Entry	Aryl Halide	Amine	Time (h)	Product	Yield (%)[a,b]	Ref.
1			8		96	86, 87
2			8		90	86, 87, 85
3			10		80	86, 87, 90
4			8		95	86, 87, 91, 82
5			10		80	86, 87
6			10		78	87, 82
7			12		65	87
8			12		78	87, 91
9			10		75	87, 82
10			12		68	87
11			10		80	82, 87
12			8		80	86

13			8		78	87
14			9		70	87
15			10		74	82
16			12		65	87
17			18		Trace	

[a] All the reactions were performed with Fe_3O_4-CuO MNPs. (20 mg), Aryl iodide (1 mmol), Amine (1.2 mmol), CS_2 (3 mmol). b Isolated yield.

pneumatic nebulizer and equipped with a charge coupled device (CCD).

Preparation of Fe_3O_4 MNPs.

5.94 g ferric chloride hexahydrate was dissolved in 200 mL highly purified water within a three neck flask. Under a nitrogen atmosphere, 2.20 g ferrous chloride tetrahydrate was added with vigorous mechanical stirring at 85 °C. Then 10 mL 30% (v/v) $NH_3.H_2O$ was added with further increased stirring speeds, and the orange-red clear solution became a black suspension immediately. The molar ratio of Fe (III) to Fe (II) in the above system was nearly 2.00. The reaction was stopped after half an hour, and the obtained suspension was cooled down to room temperature. The magnetic nanoparticles were sequentially washed with deionized water, 0.02 mol L^{-1} sodium chloride and ethanol for several times until solution was clarified quickly in the external magnetic field. The obtained black powder (Fe_3O_4 MNPs) was washed, and dried in vacuum oven.

Preparation of Fe_3O_4-CuO nanocatalyst

Magnetite nanoparticles, Fe_3O_4, (2 g) was added to a solution of copper chloride dihydrate ($CuCl_2.2H_2O$, for 5 wt % of Cu on magnetite) in H_2O (50 mL) and mechanically stirred at room temperature for 1 h. After impregnation, the suspension was adjusted to pH 12-13 by adding sodium hydroxide (1.0 M) and further stirred for 20 h. The solid was washed with distilled water (5 × 10 mL), and the resulting Fe_3O_4-CuO nanoparticles were sonicated for 10 min, washed with distilled water and subsequently with ethanol, and dried in a vacuum oven at 60 °C for 24 h. The Cu content of Fe_3O_4-CuO nanoparticles was found to be 4.50% as determined by ICP-OES.

Synthesis of *S*-aryl dithiocarbamates

Representive experimental procedure for the condensation of pyrrolidine, CS_2 and Phenyl iodide (Table 1, entry1).

In a 50 mL round-bottom flask, fitted with a magnetic stir-bar in an ice-bath, CS_2 (3 mmol) was added to pyrrolidine (1.2 mmol) and stirred for 10 min. Then, Fe_3O_4-CuO MNPs. (20 mg) and Phenyl iodide (1 mmol) was added. The reaction mixture was then heated at 130 °C. The progress of the reaction was monitored with thin-layer chromatography (TLC). After completion of the reaction (8 h), the reaction mixture was cooled to room temperature, then water (15 mL) was added and the magnetic nanocatalyst was separated from the mixture using an external magnet. The product was extracted with ethyl acetate (3 × 10 mL). Evaporation of the solvent gave a crude product that purified by simple crystallization from ethanol to provide the corresponding *S*-aryl dithiocarbamate, pyrrolidine-1-carbodithioic acid phenyl ester, as a pale yellow solid, mp 97-99 °C, FT-IR (KBr) 2935, 2842, 1565, 1461, 1269, 1120, 1005, 970, 854, 740, 674 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.97-2.06 (m, 2H), 2.10-2.19 (m, 2H), 3.81 (br, 2H), 3.95 (br, 2H), 7.41-7.53 (m, 5H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.3, 26.2, 51.0, 55.3, 129.0 (2C), 130.0, 130.9, 136.8 (2C), 203.0 ppm.

The compounds synthesized by above procedure are listed in Table 2. All of the products are known, and the structure of the products were determined from their NMR spectra and by comparison with those reported in the literature.

Table 3. Reusability study of Fe_3O_4-CuO nanocatalyst

Entry	Yield[a] %
1	96
2	94
3	90
4	88

[a] Isolated yield after each run

Conclusion

In summary, a magnetically recyclable and highly efficient Fe_3O_4–CuO nanocatalyst was designed and synthesized. The catalyst used for a mild and efficient preparation of *S*-aryl dithiocarbamates under Ullmann-type coupling reaction in solvent-free conditions without using any base or ligand. Various *S*-aryl dithiocarbamates were synthesized in good yield under benign reaction conditions. This catalyst was found to be stable and could easily seperated by an external magnet and reused for several cycles without significant loss of its activity.

Acknowledgements

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A convenient preparation of *S*-aryl dithiocarbamates from amine, carbon disulfide and aryl iodide was developed by using Fe_3O_4-CuO nanocatalyst under solvent free conditions.