



Synthesis and characterization of magnetic copper ferrite nanoparticles and their catalytic performance in one-pot odorless carbon-sulfur bond formation reactions



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ABSTRACT

In this article, we have introduced catalytic application of copper ferrite nanoparticles (CuFe₂O₄) for one-pot odorless production of aryl alkyl thioethers using thiourea and alkyl bromides in wet polyethylene glycol as a green solvent. The catalyst was also successfully applied for one-pot synthesis of symmetrical diaryl trithiocarbonates *via* the reaction of sodium sulfide, carbon disulfide and aryl iodides under heterogeneous reaction condition. Magnetic copper ferrite nanoparticles were synthesized using iron (III) chloride and copper (II) chloride, and characterized using XRD, FT-IR, AAS, and TEM analysis. The catalyst was recycled using simple magnetic separation and reused for the five consecutive runs in the reaction of iodobenzene, thiourea and benzyl bromide without appreciable loss of activity.

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1. Introduction

The choice of catalyst support plays an important role in the overall performance of the catalytic systems. Despite their handling simplicity, heterogeneous catalysts are typically less effective than their homogeneous counterparts [1]. Moreover, many of the heterogeneous catalysts are very difficult to separate from the reaction mixture by classical methods such as filtration and centrifugation. Along this line, preparation of magnetically separable catalysts based on transition metals such as palladium [2–5], cobalt [6] and copper [7–9] derivatives have been well explored in recent years. However, less attention has been focused on direct catalytic applications of magnetic nanoparticles in organic transformations [10–16]. *Ortho*-Benzoylation of phenols [10], synthesis of diselenides and ditellurides by cross coupling of Se(0) or Te(0) with aryl iodides [11], synthesis of 2,3-dihydro-2-thioxoquinazolin-4(1H)-ones [12], addition of acid chlorides to alkynes [13], *N*-monoalkylation of aromatic amines with benzylic alcohols [14], reduction of olefins [15] and synthesis of α -aminonitriles [16] are examples of direct using of Fe₃O₄ nanoparticles as a catalyst in literature. Recently, we have introduced application of paramagnetic iron oxide (Fe₃O₄)

nanoparticles as an efficient catalyst for carbon–carbon bond formation *via* the Sonogashira–Hagihara reaction under ligand-free conditions [17]. Among the several magnetic materials tested, copper ferrites have attracted wide interest as a catalyst in recent years due to synergetic catalytic effect between copper and iron sites [18]. In this regard CuFe₂O₄ nanoparticles without any functionalization have been used as a magnetically recoverable nano-catalyst in various catalytic organic transformations [19–31].

The construction of carbon–sulfur bond is one of the most important chemical reactions, since the resulting products contain important structural motifs of numerous biologically and pharmaceutically active compounds [32,33]. For example, aryl sulfide moieties are vital building blocks in the structure of some medicines for the treatment of Alzheimer, Parkinson, diabetes, and as anti HIV and anti-inflammatory [34–40]. The traditional method for the synthesis of aryl sulfides is the Ullmann-type C–S cross-coupling reaction between thiols and aryl halides. However, this reaction typically has performed under harsh reaction conditions, such as elevated temperatures (>200 °C) and required high boiling-point polar solvents such as quinoline, HMPA or *N,N*-dimethylacetamide (DMAC) that usually have toxic nature [41,42].

In order to reduce the mentioned drawbacks and providing mild reaction conditions, different transition metal catalysts such as copper [43–59], palladium [60–69], nickel [70], cobalt [71],

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indium [72,73], iron [74,75] and manganese salts [76] were developed for the coupling reaction of thiols with aryl compounds. In addition, some efforts have been made in developing of carbon–sulfur bond forming in more eco-friendly solvents such as water [77–79]. Although, significant improvement has been achieved in this area, the main limitations of current protocols are still using of volatile and foul smelling thiols with low molecular weight as the substrate that can leads to the serious safety and environmental problems.

To overcome these drawbacks, two important protocols for C–S bond construction under one-pot odorless reaction conditions reported by us. In the first report, one-pot odorless C–S bond formation *via* Michael addition reaction using thiourea and alkyl bromides was described [80]. This method was also extended for odorless thioarylation of alkyl bromides with aryl halides in the presence of copper (I) iodide in wet PEG 200 [81].

Our second protocol for one-pot carbon–sulfur bond formation, has described copper (I) iodide-catalyzed synthesis of symmetrical diaryl trithiocarbonates using the reaction of sodium sulfide, carbon disulfide and aryl halides [82].

Encouraging by our first new concept, several research groups and us have started to apply one-pot odorless thioetherification reaction using different copper or palladium catalysts and different sulfur surrogates such as thiourea [83–85], thioacetamide [86], potassium thiocyanate [87–89], thioacetate [90], potassium ethyl xanthogenate [91], sodium hydrosulfide [92], potassium 5-methyl-1,3,4-oxadiazole-2-thiolate [93], aminothiourea [94] and elemental sulfur [95,96]. However, in most of these reported methods, carbon sulfur bond formation reaction was performed under homogeneous and non-recoverable reaction conditions.

Despite the significant achievements in some of these reports, homogeneous catalysts suffer being difficult to separate from the product and problems associated with the recycling of the catalyst. This issue has paramount importance for pharmaceutically active materials, because there are typically strict guidelines to limit the levels of metals impurity in the drug substance. To the best of our knowledge, there is only one report in the literature on using of copper grafted furfural imine-functionalized mesoporous SBA-15 for one-pot thioetherification of aryl halides with thiourea and benzyl bromide in water [53].

Now in this work, we report the synthesis and characterization of CuFe_2O_4 nanoparticles as a highly recyclable and heterogeneous catalyst for the odorless thioetherification of aryl halides using alkyl halides and thiourea in wet polyethylene glycol as a green solvent. Also, the catalyst was successfully utilized for the synthesis of symmetrical diaryl trithiocarbonates from the reaction of sodium sulfide, carbon disulfide and aryl iodides under heterogeneous reaction condition. The catalyst can be easily and completely separated from the final reaction mixture by employing an external magnetic field.

2. Experimental

2.1. General procedure for the preparation of CuFe_2O_4 nanoparticles

Copper ferrite nanoparticles were prepared *via* the conventional co-precipitation method using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in an argon atmosphere. In a typical procedure a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.216 g, 8.2 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (699 mg, 4.1 mmol) in 75 ml deionized water was prepared and stirred at room temperature under continuous flow of argon atmosphere. In this condition a basic solution containing 3 g NaOH in 15 mL deionized water was added drop-wise during 10 min to the above mentioned solution under vigorous stirring. During the addition of basic solution,

black precipitate was formed immediately indicating the formation of copper ferrite nanoparticles. Then, the reaction mixture was heated to 90°C and stirred for 5 h in this temperature. Subsequently, CuFe_2O_4 magnetic nanoparticles were separated with external magnet and washed with deionized water (4×10 mL) and EtOH (4×10 mL) then dried in air oven at 80°C for overnight. Finally, the obtained nanoparticles were calcinated at 700°C for 5 h.

2.2. General procedure for thioarylation reactions

In a 5 mL flask, aryl halide (1 mmol), alkyl halide (1.1 mmol), thiourea (91 mg, 1.2 mmol), CuFe_2O_4 (12 mg, 5 mol%), K_2CO_3 (552 mg, 4.0 mmol), H_2O (0.3 mL), and PEG (2 mL) were added and stirred at 80 – 100°C for the appropriate reaction time. After completion of reaction, the mixture was cooled to room temperature and washed with 5 mL H_2O and 10 mL EtOAc. Then, after separation and evaporation of organic solvent, the crude thioethers, were purified by flash column chromatography on silica gel eluted with the appropriate mixture of (EtOAc/*n*-hexane).

2.3. General procedure for the synthesis of diaryl trithiocarbonates

To the stirring mixture of Na_2S (1.1 mmol) in DMF (2 mL), CS_2 (5 mmol) was added at room temperature and mixture was stirred for 15 min. Then, CuFe_2O_4 (12 mg, 5 mol%) and aryl iodides (2 mmol) were added to the reaction mixture and stirred at 100°C for appropriate reaction time. After completion of reaction, the reaction mixture was cooled to room temperature and extracted with EtOAc. Evaporation of the solvent yielded the crude diaryl trithiocarbonate which was purified by flash column chromatography on silica gel (EtOAc/*n*-hexane).

3. Results and discussion

CuFe_2O_4 nanoparticles were prepared without using any capping agent or surfactant *via* conventional co-precipitation of copper (II) chloride and iron (III) chloride according to the reported procedure [97]. Thanks to its magnetic nature, the CuFe_2O_4 nanoparticles conveniently collected in a side wall of reactor by using a hand-held magnet during the separation and washing processes. Then, the catalyst was characterized using various physicochemical techniques including XRD, TEM and FT-IR analysis. Also, the copper and iron contents were measured by atomic absorption spectroscopy. Based on the AAS analysis the contents of Cu and Fe in the prepared CuFe_2O_4 nanoparticles were found to be 26.4 wt% (4.2 mmolCu/g) and 32.3 wt%, respectively.

The structure of the synthesized CuFe_2O_4 nanoparticles was confirmed using X-ray diffraction analysis. The XRD pattern of the as-prepared CuFe_2O_4 nanoparticles was in good agreement with the standard of cubic structure of copper ferrite (JCPDS 77-0010) (Fig. 1). In addition, the strong and sharp reflection peaks in XRD pattern prove the crystalline nature of the prepared CuFe_2O_4 nanoparticles.

The structure of CuFe_2O_4 magnetic nanoparticles was further characterized with FT-IR spectroscopy. The presence of stretching mode for Fe–O band at 575 cm^{-1} , Cu–O at 438 cm^{-1} and the broad peak at 3432 cm^{-1} for surface O–H groups confirmed the structure of prepared copper ferrite nanoparticles (see supporting information).

TEM image was also used to further characterization of the morphology and structure of CuFe_2O_4 nanoparticles. As can be seen in Fig. 2, CuFe_2O_4 nanoparticles are mostly spherical and cubic,

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