



# Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-copper sucrose xanthate as a green nanocatalyst for N-, O- and S-arylation

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Formation of C(sp<sup>2</sup>)-X bonds was carried out using a Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-copper(I) sucrose xanthate nanoparticle catalyst with the aid of the copper(I) xanthate moiety in the catalyst which was prepared from the reaction between sucrose and carbon disulfide through an alkaline medium via the traditional Zeise approach. Various techniques were employed for the characterization of these novel nanoparticles. Three sorts of heteroatoms, N, O and S, successfully underwent heteroatom arylation to produce secondary or tertiary amines, ethers and thioethers, respectively.

## KEYWORDS

carbon-heteroatom coupling, copper, sucrose, Ullmann coupling, xanthate

## 1 | INTRODUCTION

Incorporations of the three most common heteroatoms (X: N, O and S) into organic frameworks specially in C(sp<sup>2</sup>-aromatic)-X bond systems has gained attention owing to a wide variety of applications such as pharmaceutical, polymer and synthetic usages.<sup>[1]</sup> Ullmann coupling has been introduced as the best way for production of pharmaceutical and natural building blocks. During the last few decades, C-X cross-coupling has been developed using various transition metals such as Pd, Ni or Cu as appealing catalysts, Cu being the most economically justifiable.<sup>[2]</sup> Copper-based materials have attracted considerable attention due to the stability of their varied oxidation forms from 0 to +3 in various transformation processes. As an outcome, this metal can be easily associated with some fields in organometallic chemistry.

During the past 20 years many endeavours have been reported for the improvement of catalysts and media.<sup>[2-4]</sup> Achieving a sustainable catalyst demands a recoverable support like magnetic nanoparticles, the nanoscale benefits of which have previously been revealed.<sup>[5]</sup> Design of a stable core meets the demand of a strict shell between the main linker and magnetic part. Among organic linkers,

sugars are considered less harmful and could be used as individual promoters to interact with copper. For this purpose, various hydroxyl sites of a sugar can be altered into dithiocarbonates through the Zeise method. The dithiocarbonate group with respect to general yellowish orange colour is also called a xanthate. The long history of xanthates as sulfur analogues goes back two centuries. One century later, Brandenberger synthesized a new polyxanthate called cellophane of cellulose.<sup>[6]</sup> Continuing such trends, firstly Mikhlin and co-workers developed a new strategy for producing copper xanthate in colloidal phase and nanoscale size and demonstrated that copper occurs as Cu(I).<sup>[7]</sup>

As a review of previous works, many procedures have been developed for Ullmann coupling as the best way for the production of pharmaceutical and of natural building blocks. Among them, copper salts<sup>[8,9]</sup> for aryl ethers, Pd@IL-PMO,<sup>[10]</sup> copper(II) sulfate,<sup>[11]</sup> [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub>/ligand,<sup>[12]</sup> CuI/HBF<sub>4</sub>,<sup>[13]</sup> IMes-Cu-Cl,<sup>[14]</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O,<sup>[15]</sup> FeCl<sub>3</sub>·6H<sub>2</sub>O/L-proline,<sup>[16]</sup> copper(II) acetate<sup>[17]</sup> and FeCl<sub>2</sub>/CuO<sup>[18]</sup> for aryl thioethers are examples of catalysts.

Herein, in continuation of our research on the preparation of new recoverable magnetic nanoparticles

functionalized with sugars and their applications in organic synthesis,<sup>[5]</sup> we report an efficient method for synthesis of the novel Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-copper(I) sucrose xanthate (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX) and an investigation of its application for carbon-heteroatom (N, O, S) cross-coupling reactions.

## 2 | EXPERIMENTAL

### 2.1 | General

The solvents and starting materials were commercially selected of synthesis grade and purchased from Merck and Acros. Fourier transform infrared (FT-IR) spectra were collected with a Nicolet IR100 FT-IR spectrometer in the wavenumber range 400–4000 cm<sup>-1</sup> using spectroscopic-grade KBr. The melting points of products were determined using a Barnstead Electronics 9100. The <sup>1</sup>H NMR (500 MHz) spectra were recorded using a Bruker Avance DPX-500NMR spectrometer with samples in CDCl<sub>3</sub> as solvent. The morphology of the catalyst was studied using scanning electron microscopy (SEM; Philips XL 30 and S-4160) with coated gold equipped with energy-dispersive X-ray (EDX) spectroscopy capability. Powder X-ray diffraction (XRD) patterns were recorded at room temperature with a Philips X-Pert 1710 diffractometer using Co K $\alpha$  radiation ( $\lambda = 1.78897 \text{ \AA}$ ) at a voltage of 40 kV and current of 40 mA to define the crystalline structure of the catalyst nanoparticles. Data were collected from 10° to 90° (2 $\theta$ ) with a scan speed of 0.04° s<sup>-1</sup>. The magnetic properties were measured with a vibrating magnetometer/alternating gradient force magnetometer (MD Co., Iran, www.mdk-magnetic.com). Thermogravimetric analysis (TGA) was performed using a thermal

analyser with a heating rate of 20°C min<sup>-1</sup> over the temperature range 25–900°C under flowing compressed nitrogen (as inert gas).

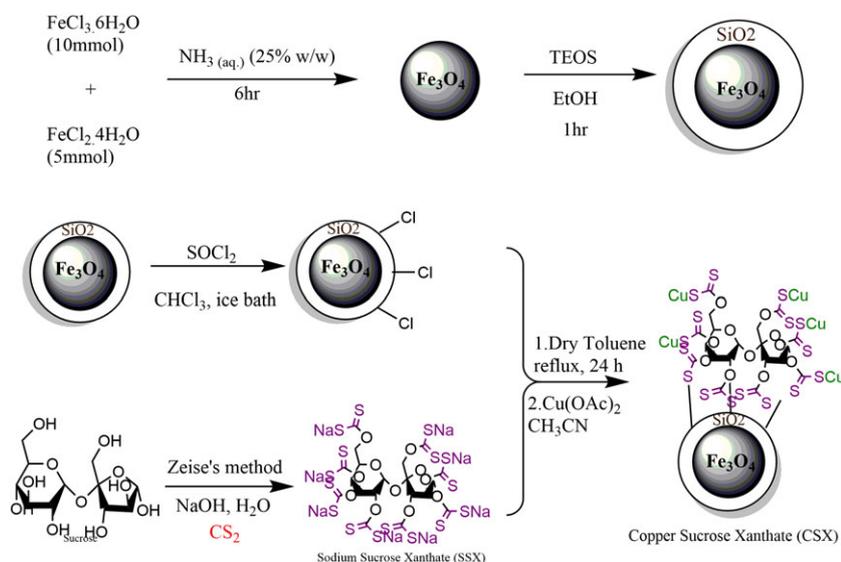
### 2.2 | Catalyst preparation

#### 2.2.1 | Preparation of chlorinated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles

Experimentally, in a typical procedure, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared through a previously reported method from iron(II) and iron(III) salts as sources in a strongly basic medium (NH<sub>3</sub> 25% standard solution), with dropwise addition of ammonia into an equimolar solution of iron(II) and iron(III). Then the solution was heated to 80°C for 6 h to complete the procedure of formation and finally washing was done with distilled water to achieve pure Fe<sub>3</sub>O<sub>4</sub> in brown to black colour.<sup>[19]</sup> The next step was carried out to form a silica shell using tetraethyl orthosilicate (TEOS) in basic aqueous medium with pH of around 11.<sup>[19]</sup> After neutralization of solution and decanting using an external magnet, the shell was chlorinated using thionyl chloride (SOCl<sub>2</sub>) in dried CHCl<sub>3</sub>. Then, the resulting product was washed with dry CHCl<sub>3</sub> and dried under vacuum at 60°C for 2 h for further reaction.

#### 2.2.2 | Preparation of sodium sucrose xanthate (SSX)

SSX was prepared using the Zeise method. An amount of 40 mmol of sodium hydroxide was added to a solution of 5 mmol of sucrose in 25 ml of hot water and stirred for 30 min at 80°C. Then, CS<sub>2</sub> (40 mmol) was added dropwise to the mixture and heated for 24 h at 80°C. The colour of



SCHEME 1 Catalyst preparation

the solution gradually became yellow and then towards the completion of the reaction it changed to orange. The product was then dried at 100°C for 3 h and the resulting orange-red solid had a sharp sulfur odour.

### 2.2.3 | General procedure for preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX

Chlorinated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (0.5 g) was added to a solution of SSX (3 mmol, 3.378 g) in dried toluene (10 ml) and then refluxed for 24 h. Afterwards, the greenish-black solid was magnetically separated and washed with water to remove excess SSX and dried at room temperature under vacuum. Subsequently, according to Mikhlín's instruction, in 8 ml of acetonitrile-methanol (4/1 v/v), the synthesized SSX (0.5 g) was reacted with 1 mmol of copper(II) acetate. The mixture has heated for 4 h at 70°C and the resulting greenish-black solid (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX) was decanted using an external magnet, washed two times with 5 ml of deionized water and dried at room temperature under vacuum.

### 2.3 | General procedure for C-X cross-coupling

To a stirred solution of phenylboronic acid (1 mmol) and aniline (N) or phenol/benzyl alcohol (O) or thiophenol(S) (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was added 50 mg of catalyst and refluxed (at 40°C) for 20 h. Then, the catalyst was separated using an external magnet and the pure product was obtained with a non-flash silica gel column.

## 3 | RESULTS AND DISCUSSION

The characterization of the catalyst was performed using several techniques: FT-IR spectroscopy, XRD, vibrating sample magnetometry (VSM), SEM-EDX, TGA and inductively coupled plasma (ICP) analysis. Scheme 1 illustrates the synthetic method of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX.

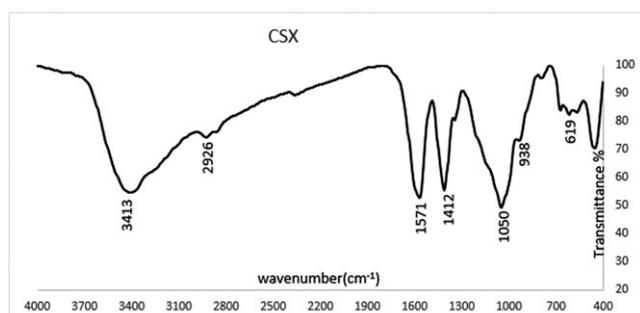


FIGURE 1 FT-IR spectrum of CSX nanoparticles

As can be seen in Figure 1, the major peaks appeared at 563 cm<sup>-1</sup> (Fe–O stretching), 619 cm<sup>-1</sup> (Cu–S stretching), 1050 cm<sup>-1</sup> (Si–O stretching), 1345 cm<sup>-1</sup> (Cu–S–C=O stretching), 1412 cm<sup>-1</sup> (Si–O stretching), 1571 cm<sup>-1</sup> (dixanthogene) and 3413 cm<sup>-1</sup> (hydroxyl O–H).

The crystal structure of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX was confirmed from its XRD pattern (Figure 2). The characteristic peaks are compatible with the standard Fe<sub>3</sub>O<sub>4</sub> (corresponding to JCPDS 75-0033 reference)<sup>[20]</sup> and the crystal structure of pure Fe<sub>3</sub>O<sub>4</sub> remains unchanged after immobilization of Cu. The broad peak appearing at 21.46° is attributed to Si.

The magnetism of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX nanoparticles was analysed via VSM in the range –10 000 to +10 000 Oe. From Figure 3, the saturation magnetization is 10.4 emu g<sup>-1</sup> and, as shown in Figure 3, the *M(H)* hysteresis loop was completely reversible. Hence, these results indicate that the nanoparticles have superparamagnetic behaviour.

The Figure 4a shows SEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX nanoparticles. According to the images, the surface morphology of the nanoparticles is uniform. The average size of the nanoparticles was estimated at around 50 nm (spherical shape) with the least possible agglomeration

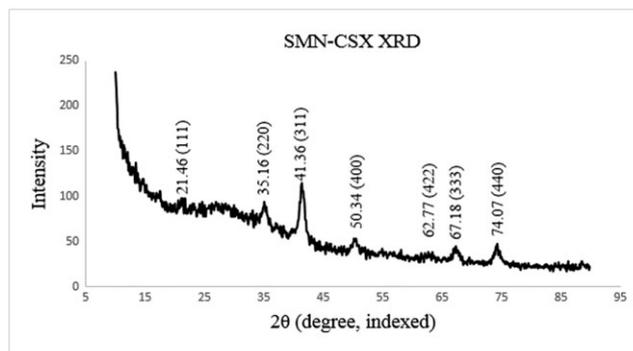


FIGURE 2 XRD pattern for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX nanoparticles

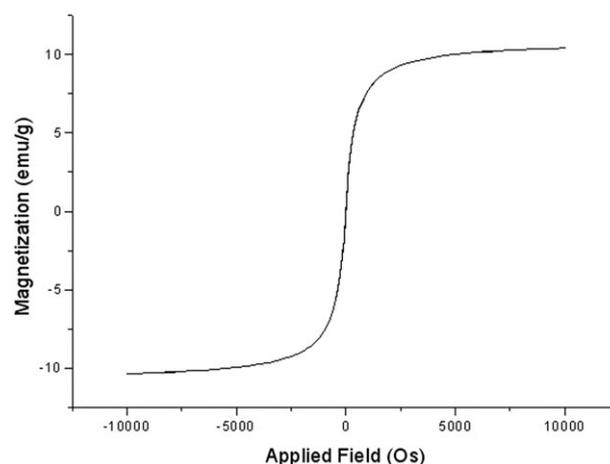
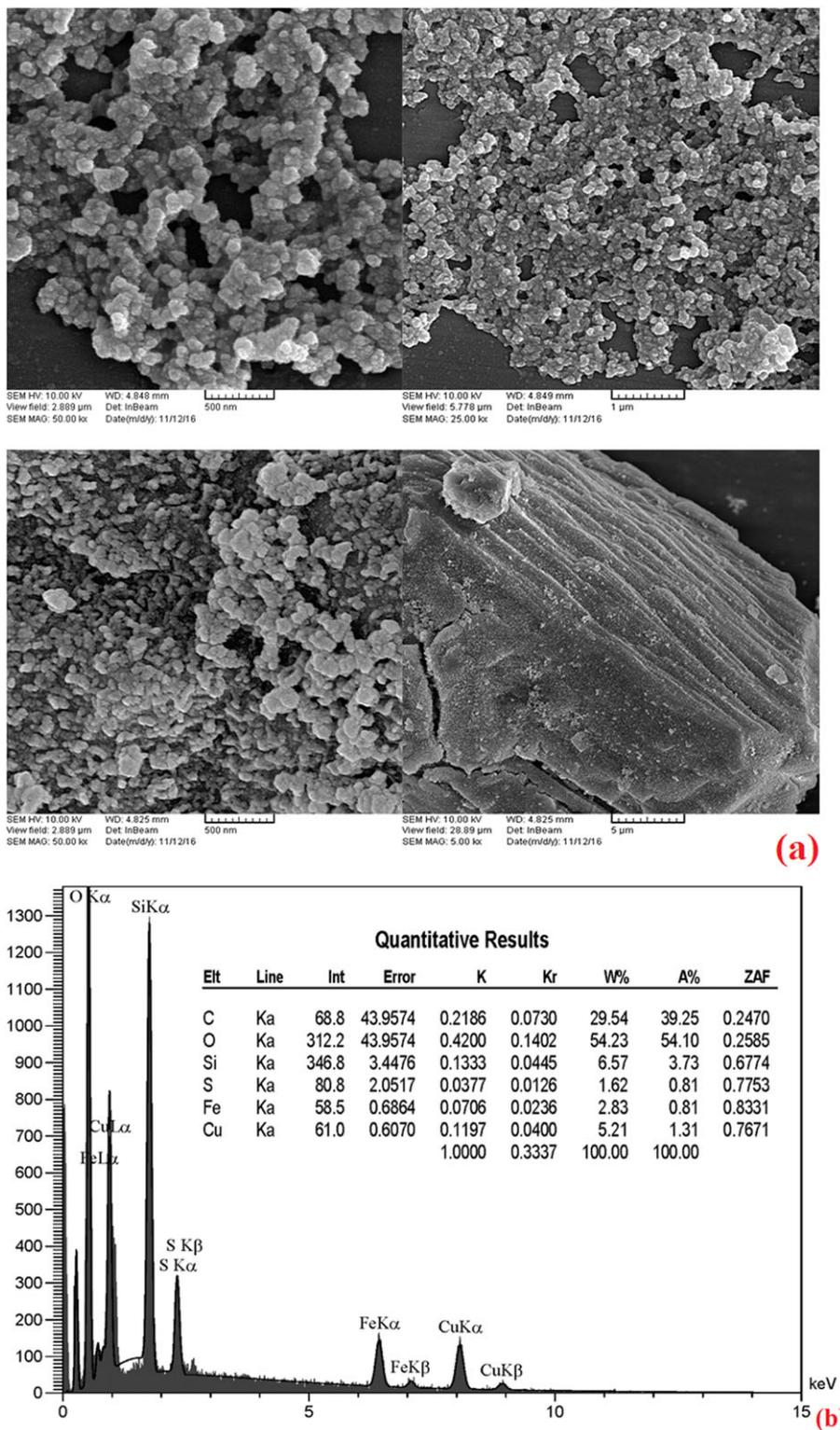


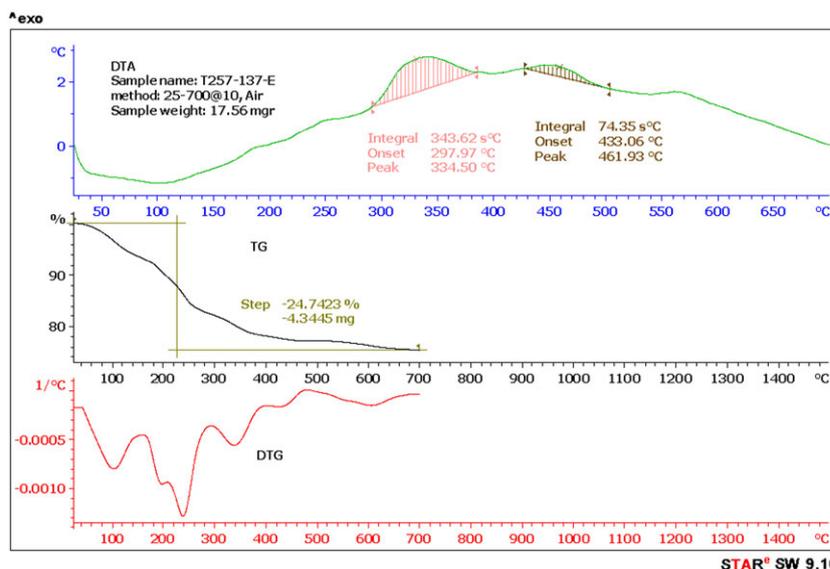
FIGURE 3 VSM diagram of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX nanoparticles



**FIGURE 4** (a) SEM images and (b) EDX analysis of  $\text{Fe}_3\text{O}_4@SiO_2\text{-CSX}$  nanoparticles

as shown in 500 nm scaled SEM image (Figure 4a). Also, the presence of sulfur and copper as an evidence for successful immobilization of SSX and Cu(II) cation onto the primary  $\text{Fe}_3\text{O}_4@SiO_2$  was confirmed via EDX analysis (Figure 4b).

The next measurement was that of the amount of organic material grafted on the primary  $\text{Fe}_3\text{O}_4@SiO_2$ . TGA revealed that about 24.74% (w/w) of catalyst mass is lost between 100 and 650°C and this result is indicative of the mass percentage of organic motif joined to the

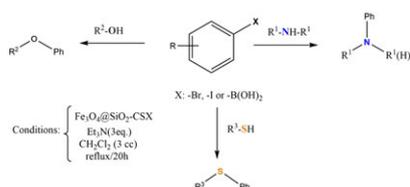


**FIGURE 5** TGA/DTG/DTA curves of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-CSX}$  nanoparticles

surface of catalyst nanoparticles. Such decrease in mass is completely a result of degradation of sugar and linked  $\text{CS}_2$  as organic motifs in the nanoparticles (Figure 5).

To provide validated evidence of the remaining copper in the synthesis step and after four catalytic runs, ICP analysis was performed. ICP measurements revealed that there are 0.345 and 0.170 mmol of copper per gram of catalyst before and after four repeat reactions, respectively. These results showed that the amount of copper linked on the nanoparticles has noticeably decreased and around half of the initial copper was released after the reaction; however, it is worth noting that the synthesized catalyst is still reliable comparing with other heterogeneous copper-based catalysts. It is worthwhile to mention the role of copper as catalyst in C–X coupling through oxidative addition and reductive elimination. Only the nanoparticles from the last step of interaction of copper with xanthate can play the role of desired catalyst, and not those of earlier steps of the preparation without copper.

Initially, to evaluate the catalytic efficiency of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-CSX}$ , C–X cross-coupling reactions between aniline/phenol/thiophenol and phenylboronic acid were chosen as model reactions (Scheme 2) and the influences of solvent, amount of catalyst, base, temperature and reaction time were investigated to develop optimized conditions.



**SCHEME 2** Model reactions for C–X cross-coupling

The coupling reactions did not occur in the absence of the catalyst and base, so catalyst and base played an important role in the transformation (Table 1). When we used  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-CSX}$  as catalyst and  $\text{K}_2\text{CO}_3$  as base, the desired products were obtained in moderate yields. When other bases such as pyridine,  $\text{Et}_3\text{N}$ , DBU, DBN,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaOH}$  and  $\text{KOH}$  were used, the best yield was ultimately afforded by  $\text{Et}_3\text{N}$ . Among the solvents, the use of refluxing  $\text{CH}_2\text{Cl}_2$  as solvent offered the best results. With regard to the amount of catalyst, using 50 mg of  $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-CSX}$  was sufficient and using a greater amount was ineffective. Surprisingly, when using aryl halides (phenyl bromide and phenyl iodide) instead of phenylboronic acid, the yield of the reaction decreased obviously. Such a decrease is theoretically because of the initial insertion pace that naturally has a competition between C–B and C–X (X: Br or I) bonds. The highest yields for  $\text{Et}_3\text{N}$  as base proved the preferable aspect of the present technique because of its easily volatile nature meaning it can smoothly be removed at temperatures lower than boiling points of liquid products.

From a literature survey, some results for previously reported similar C–X couplings are presented in Table 2.

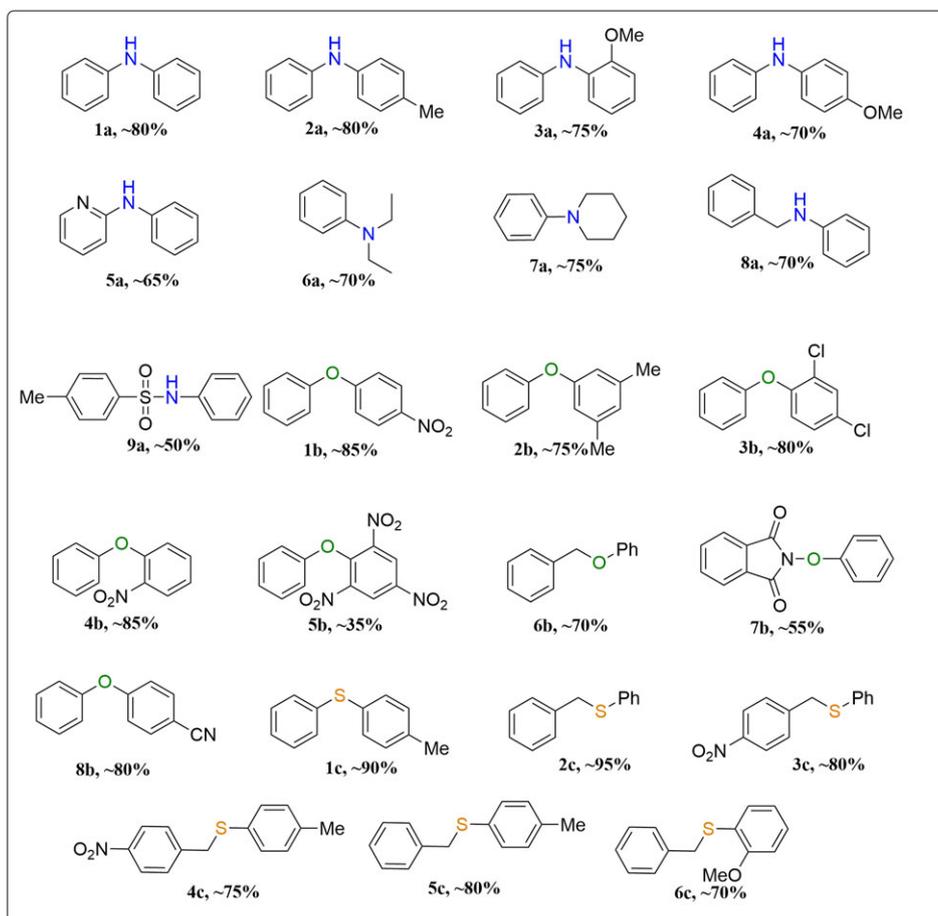
Under the optimized conditions, the C–X cross-coupling of arylamines, phenols (benzyl alcohol) and thiophenols was investigated. The reaction proceeded with both electron-donating and electron-withdrawing nucleophiles for obtaining the corresponding amines, ethers and thioethers. Scheme 3 shows that the N-arylation reaction proceeded smoothly from anilines containing different electron-donating groups (**2a**). However, target products could not be synthesized in considerable yield for electron-deficient aromatic systems (**9a**). This protocol efficiently coupled aliphatic amines with phenylboronic acid to provide the desired products in

**TABLE 1** Optimizing reaction conditions in the C–X cross-coupling catalysed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX

Entry	Base	Catalyst (mg)	Solvent (3 cm <sup>3</sup> )	Temp. (°C)	Time (h)	Yield (%) ± 2.5%
1	—	—	CH <sub>2</sub> Cl <sub>2</sub>	40	20	0, 0, 0 <sup>a</sup>
2	Et <sub>3</sub> N	20	1,4-Dioxane	70	20	70, 60, 75
3	K <sub>2</sub> CO <sub>3</sub>	20	1,4-Dioxane	70	20	55, 50, 65
4	K <sub>2</sub> CO <sub>3</sub>	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	45, 30, 40
5	Et <sub>3</sub> N	20	CH <sub>3</sub> CN	82	20	45, 20, 40
6	Et <sub>3</sub> N	20	THF	66	20	65, 40, 55
7	Et <sub>3</sub> N	20	EtOAc	77	20	40, trace, 40
8	Et <sub>3</sub> N	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	80, 65, 85
9	Et <sub>3</sub> N	20	CH <sub>2</sub> Cl <sub>2</sub>	40	30	75, 65, 85
10	Et <sub>3</sub> N	20	CH <sub>2</sub> Cl <sub>2</sub>	40	40	75, 65, 85
11	Et <sub>3</sub> N	20	CH <sub>2</sub> Cl <sub>2</sub>	40	10	70, 55, 70
12	Pyridine	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	65, 40, 50
13	KOH	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	40, 60, 70
14	NaOH	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	40, 50, 70
15	Na <sub>2</sub> CO <sub>3</sub>	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	30, 20, 40
16	NaHCO <sub>3</sub>	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	45, trace, 30
17	K <sub>3</sub> PO <sub>4</sub>	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	35, 20, 40
18	DBU	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	65, 45, 65
19	DBN	20	CH <sub>2</sub> Cl <sub>2</sub>	40	20	70, 55, 65
20	Et <sub>3</sub> N	30	CH <sub>2</sub> Cl <sub>2</sub>	40	20	60, 37, 70
<b>21</b>	<b>Et<sub>3</sub>N</b>	<b>50</b>	<b>CH<sub>2</sub>Cl<sub>2</sub></b>	<b>40</b>	<b>20</b>	<b>80, 70, 90</b>
22	Et <sub>3</sub> N	75	CH <sub>2</sub> Cl <sub>2</sub>	40	20	80, 70, 90
23	—	50	CH <sub>2</sub> Cl <sub>2</sub>	40	20	trace, 0, 0
24	Et <sub>3</sub> N	—	CH <sub>2</sub> Cl <sub>2</sub>	40	20	0, 0, 0
25	Et <sub>3</sub> N	50	Solvent-free	40	20	15, 0, 20

<sup>a</sup>Yield: C–N (Ph<sub>2</sub>NH), C–O ((Ph-CH<sub>2</sub>)–O–Ph), C–S (Ph–S–(C<sub>6</sub>H<sub>4</sub>–Me)).**TABLE 2** Survey of some of previously reported C–X couplings

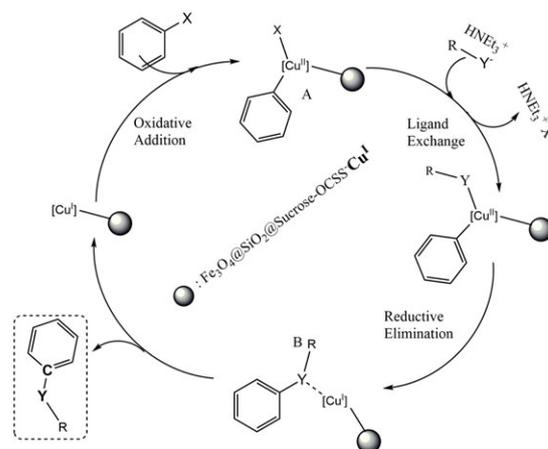
Entry	Substrate	Catalyst	Base	Solvent/temp.	Yield (%)
1	Ph-I/imidazolePh-I/Ph-OH Ph-I/Ph-SH	CuI/ <i>N,N'</i> -dioxide ligands <b>Note:</b> homogeneous catalyst	Cs <sub>2</sub> CO <sub>3</sub>	DME/80°C	95 <sup>[2]</sup> 98 95
2	<i>p</i> -Tol-B(OH) <sub>2</sub> /4-NH <sub>2</sub> -Pyridine <i>p</i> -Tol-B(OH) <sub>2</sub> /2-NH <sub>2</sub> -Pyridine	Cu (OAc) <sub>2</sub>	Pyridine	CH <sub>2</sub> Cl <sub>2</sub> /r.t.	74 <sup>[21]</sup> 23
3	Cyclohexyl-SH/Ph-B(OH) <sub>2</sub>	Cu(OAc) <sub>2</sub> /4 Å MS	Pyridine	—	88 <sup>[22]</sup>
4	Ph-Br/Ph-SH Ph-I/Ph-SH	Pd@IL-PMO	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O/100°C	88 <sup>[10]</sup> 96
5	Ph-B(OH) <sub>2</sub> /Ph-SH	CuSO <sub>4</sub> /10-Phen.H <sub>2</sub> O	<i>n</i> -Bu <sub>4</sub> N–OH	EtOH/r.t.	83 <sup>[11]</sup>
6	Ph-I/Ph-SH	IMes-Cu-Cl	LiOBu <sup>t</sup>	Toluene/120°C	82 <sup>[14]</sup>
7	Ph-I/Ph-SH	NiCl <sub>2</sub> .6H <sub>2</sub> O	KOH	TBAB	99 <sup>[15]</sup>
8	4-Ac-C <sub>6</sub> H <sub>4</sub> -I/Ph-SH	FeCl <sub>3</sub> .6H <sub>2</sub> O/L-Proline	KOH	TBAB/H <sub>2</sub> O/130°C	95 <sup>[16]</sup>
9	6-Iodoimidazo[1,2- <i>a</i> ]pyridine/Ph-SH 6-Iodoimidazo[1,2- <i>a</i> ]pyridine/imidazole	FeCl <sub>2</sub> .4H <sub>2</sub> O/CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMF/135°C	60 <sup>[18]</sup>  50



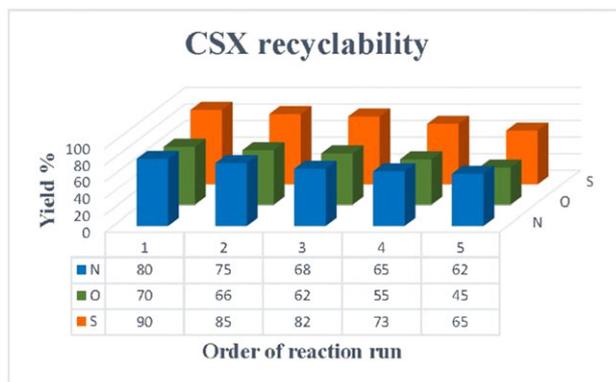
**SCHEME 3** Scope of the three types of C-X cross-coupling reactions

good yields. Under the optimized conditions, sulfonamide was reacted with phenylboronic acid to produce the desired product. Also, having identified the optimal conditions, the scope and versatility of this method was extended to the reaction of various phenols with phenylboronic acid. Generally, phenols having electron-withdrawing groups gave the related product in excellent yields in comparison to electron-donating ones. Although 4-nitrophenol gave high yield of cross-coupled products, the more sterically hindered 2,4,6-trinitrophenol (picric acid) generated only in moderate amounts the O-arylation product. However, benzyl alcohol produced target products in good yield. Notably, *N*-hydroxyphthalimide could be reacted with phenylboronic acid to afford the desired product in moderate yield. Moreover, we investigated the catalytic efficiency of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CSX}$  for coupling of phenylboronic acid and various iodobenzene derivatives with thiols. Excellent conversion was obtained for these reactions between various thiols and phenylboronic acid (**1c–3c**) and iodobenzene derivatives having both electron-donating and electron-withdrawing groups (**4c–6c**). It should be noted that there was no coupling between currently used nucleophiles and aryl chlorides.

The proposed mechanism for the coupling reactions is depicted in Scheme 4. The oxidative addition of aryl halide to  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CSX}$  occurs to give Cu intermediate A. Then, deprotonation of amine/phenol/thiophenol and ligand exchange produce Cu intermediate B. Finally, the desired cross-coupled product is easily provided by reductive elimination.



**SCHEME 4** Possible suggested mechanism of C-X coupling



**FIGURE 6** Catalyst reusability

Sustainability is one of the important properties of a heterogeneous catalyst. So, this character of the synthesized nanocatalyst was investigated in the model reactions. It was observed that the catalyst can be reused at least five times without significant loss in yields of the products **1a** (N), **6b** (O) and **1c** (S) (Figure 6). Previous work has been carried out concerning the Ullmann reaction applying different metal-based catalysts.<sup>[23–29]</sup>

## 4 | CONCLUSIONS

In summary, we used xanthate hook to stabilize a copper-based catalyst according to Mikhlin's instruction and the catalyst was completely characterized. Then, the performance of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CSX nanoparticles as a heterogeneous catalyst was investigated in three types of C–X cross-coupling reactions. The desired products were obtained good to high yields. Also, the catalyst was reliable after being used several times. It is a noteworthy advantage that the current catalyst utilizes less amount of copper when compared with previous reports involving stoichiometric amounts for each coupling reaction. Such an advantage is accompanied with drawbacks like copper leaching during recycling steps and long reaction times.

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