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Note

A simple and green synthesis of diaryl sulfides catalyzed by an MCM-41-immobilized copper(I) complex in neat water

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The heterogeneous carbon–sulfur bond formation reaction of aryl iodides with potassium thiocyanate was achieved in neat water at 130 °C by using 5 mol% MCM-41-immobilized bidentate nitrogen/CuCl complex [MCM-41-2N–CuCl] as catalyst and Cs_2CO_3 as base, yielding a variety of diaryl sulfides in moderate to high yields. This heterogeneous copper catalyst can be easily prepared by a simple two-step procedure from commercially available and cheap reagents and recovered by a simple filtration and reused for 10 cycles without loss of catalytic activity.

1. Introduction

Recently, increasing attention has been paid to the development of environmentally benign organic transformations for the construction of complex molecules [1–4]. The aryl–sulfur bonds proverbially exist in many molecules that are of biological, pharmaceutical and materials interest [5–11]. For example, diaryl sulfide functionalities have been found in numerous drugs with a broad spectrum of therapeutic activities such as antidiabetes, anti-inflammatory, anti-Alzheimer's, anti-Parkinson's, anticancer, and anti-HIV [12,13]. Traditional methods for the synthesis of aryl–sulfur bonds often require harsh reactions. For instance, coupling of copper thiolates with aryl halides take place in polar solvents such as HMPA, and at elevated temperature around 200 °C. Reduction of aryl sulfones or aryl sulfoxides requires strong reducing agents such as DIBAL-H or $LiAlH_4$ [14–16]. The development of efficient methods for the formation of aryl–sulfur bonds has been a subject of interest in synthetic chemistry since Migita first reported the palladium-catalyzed cross-coupling of aryl halides with thiols [17,18]. A wide range of transition metals was used to catalyze this coupling reaction, including palladium [19–24], nickel [25,26], cobalt [27], copper [28–32], and indium [33,34]. Among these methods, the copper-catalyzed cross-coupling is highly attractive due to the relatively low cost and environmentally negative influence of the process. Although these copper-catalyzed cross-coupling reactions of aryl halides with thiols are highly efficient, the problem with homogeneous catalysis is the difficulty to separate the copper catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. In addition, homogeneous catalysis might result in unacceptable copper contamination of the desired isolated product, which is a particularly significant drawback for its application in the pharmaceutical industry. From the standpoint of environmentally benign organic synthesis, the design of a green chemical method for the formation of aryl–sulfur bonds is considered of high practical value.

Over the last decade there has been an increasing interest in the search for more sustainable chemical processes. In this context, the use of nontoxic chemicals, renewable reagents and environmentally friendly solvents, among which water is the most benign one, is a most valuable feature for the design of a "green" chemical protocol. Recently, the use of water as solvent in organic reactions has attracted much attention due to the low cost, nontoxicity, safety, availability, and greater chemo-selectivity compared with organic solvents [35–38]. Carril et al. reported the S-arylation of thiophenol derivatives with aryl halides leading to diaryl sulfides catalyzed by a combination of a copper salt and a 1,2-diamine

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derivative using exclusively water as the solvent, the water solution containing the copper complexes can be reused for only three times [39]. Recently, Zhou et al. reported a highly efficient protocol of C–S bond formation between aryl halides and potassium thiocyanate in water using 10 mol% $CuCl_2$/1,10-phenanthroline as a catalytic system and $(n\text{-Bu})_4NF$ as a PTC, no the recovery and reutilization of the aqueous medium containing the active catalyst was described [40].

In spite of tremendous effort dedicated to the immobilization of homogeneous palladium complexes over the last two decades [41,42], very few examples of carbon–carbon bond or carbon–heteroatom bond formation reactions catalyzed by heterogeneous copper catalysts have appeared [43–48]. So, the development of a stable heterogeneous copper catalyst that allows for highly efficient C–S bond formation reactions of a wide range of aryl halides is worthwhile. Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [49]. MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area $>700\ m^2\ g^{-1}$ [50]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [51–53]. To date, some palladium and rhodium complexes on functionalized MCM-41 support have been prepared and successfully used in organic reactions [54–60]. Very recently, we reported the synthesis of the first MCM-41-immobilized bidentate nitrogen/CuI complex and found that it is a highly efficient and recyclable heterogeneous catalyst for the homo- and heterocoupling of terminal alkynes [46]. However, to the best of our knowledge, no C–S bond formation reaction between aryl halides and potassium thiocyanate catalyzed by immobilization of copper in MCM-41 has been described in the open literature. In continuing our efforts to develop greener synthetic pathways for organic transformations, herein we wish to report an efficient, heterogeneous C–S bond formation reaction between aryl iodides and potassium thiocyanate catalyzed by an MCM-41-immobilized bidentate nitrogen/CuCl complex in neat water.

2. Experimental

2.1. General remarks

All chemicals were reagent grade and used as purchased. The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane was generally used as eluent. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. ^1H NMR spectra (400 MHz) were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Copper content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction was obtained on Damx-rA (Rigaka). Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. GC analysis was performed on an SRI 8610C equipped with a fused silica capillary column. The mesoporous material MCM-41 was easily prepared according to a literature procedure [61].

2.2. Preparation of the catalyst

2.2.1. Preparation of MCM-41-2N

A solution of 2.31 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h to obtain 3.474 g of hybrid material MCM-41-2N. The nitrogen content was found to be 2.19 mmol/g by elemental analysis.

2.2.2. Preparation of MCM-41-2N–CuCl

In a small Schlenk tube, 1.0 g of MCM-41-2N was mixed with 0.1 g (1.0 mmol) of CuCl in 10 mL of dry DMF. The mixture was stirred at room temperature for 7 h under an argon atmosphere. The solid product was filtered by suction, washed with DMF and acetone and dried at 60 °C/26.7 Pa under Ar for 5 h to give 1.086 g of a pale blue copper complex (MCM-41-2N–CuCl). The nitrogen and copper content was found to be 1.77 mmol/g and 0.46 mmol/g, respectively.

2.3. General procedure for the synthesis of diaryl sulfides

To a resealable Schlenk tube, was added Cs_2CO_3 (2.0 mmol), KSCN (1.5 mmol) and MCM-41-2N–CuCl (110 mg, 0.05 mmol), and the reaction vessel was fitted with a rubber septum. The vessel was evacuated and back-filled with argon and this evacuation/back-fill procedure was repeated one additional time. The aryl iodide (1.0 mmol) and water (3 mL) were then added under a stream of argon. The reaction tube was quickly sealed and the contents were stirred while heating in an oil bath at 130 °C for 48 h. After completion of the reaction, the reaction mixture was cooled to room temperature, extracted with ethyl acetate (3 × 5 mL), and filtered. The MCM-41-2N–CuCl complex was washed with distilled water (2 × 5 mL), ethyl acetate (2 × 5 mL), and Et_2O (2 × 5 mL) and reused in the next run. The extract was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate = 50:1 to 10:1) to provide the desired product.

2.3.1. Diphenyl sulfide, **2a** [40]

Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.41–7.27$ (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 135.8, 131.1, 129.2, 127.1$.

2.3.2. Di-p-tolyl sulfide, **2b** [40]

Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.15$ (d, $J = 8.0$ Hz, 4H), 7.01 (d, $J = 8.0$ Hz, 4H), 2.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 136.9, 132.7, 131.1, 129.9, 21.1$.

2.3.3. Di-o-tolyl sulfide, **2c** [40]

White solid. ^1H NMR($CDCl_3$, 400 MHz): $\delta = 7.24$ (d, $J = 8.4$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 2H), 7.10 (t, $J = 7.2$ Hz, 2H), 7.05 (d, $J = 7.6$ Hz, 2H), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 138.9, 134.3, 131.1, 130.5, 127.1, 126.7, 20.4$.

2.3.4. 4,4′-Dimethoxy diphenyl sulfide, **2d** [62]

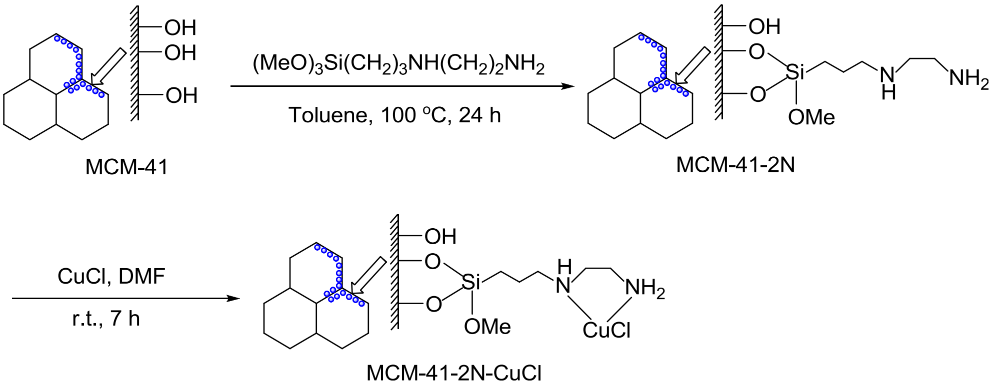
Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.20$ (d, $J = 8.8$ Hz, 4H), 6.76 (d, $J = 8.8$ Hz, 4H), 3.71 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 158.5, 132.2, 126.9, 114.3, 54.9$.

2.3.5. 2,2′-Dimethoxy diphenyl sulfide, **2e** [40]

White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.27–7.22$ (m, 2H), 7.05 (dd, $J = 1.6$ Hz, $J = 7.6$ Hz, 2H), 6.92–6.85 (m, 4H), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 157.8, 132.0, 128.4, 122.6, 121.2, 110.8, 55.9$.

2.3.6. 3,3′-Dimethoxy diphenyl sulfide, **2f** [40]

White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.25$ (t, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.93 (s, 2H), 6.83–6.80 (m, 2H), 3.80 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 160.1, 136.7, 130.1, 123.4, 116.3, 113.0, 55.3$.



Scheme 1. Preparation of MCM-41-2N–CuCl complex.

2.3.7. 4,4′-Dichloro diphenyl sulfide, ***2g*** *[62]*

Colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.29$–7.21 (m, 8H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 133.9, 133.5, 132.3, 129.5$.

2.3.8. 4,4′-Dibromo diphenyl sulfide, ***2h*** *[40]*

White solid. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.45$ (d, $J = 8.4$ Hz, 4H), 7.21 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 134.5$, 132.6, 132.4, 121.5.

2.3.9. 4,4′-Difluoro diphenyl sulfide, ***2i*** *[40]*

Colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.24$–7.20 (m, 4H), 6.92 (t, $J = 8.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 162.2$ (d, $^1J_{\mathrm{CF}} = 246.0$ Hz), 133.0 (d, $^3J_{\mathrm{CF}} = 8.0$ Hz), 131.1 (d, $^4J_{\mathrm{CF}} = 3.0$ Hz), 116.4 (d, $^2J_{\mathrm{CF}} = 22.0$ Hz).

2.3.10. 4,4′-Dinitro diphenyl sulfide, ***2j*** *[40]*

Yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.14$ (d, $J = 8.8$ Hz, 4H), 7.42 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 141.7$, 130.1, 125.1, 123.6.

2.3.11. 2,2′-Dinitro diphenyl sulfide, ***2k*** *[40]*

Yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.10$ (d, $J = 8.0$ Hz, 2H), 7.58–7.48 (m, 4H), 7.31 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 149.4$, 133.8, 133.7, 131.5, 128.7, 125.5.

2.3.12. 3,3′-Ditrifluoromethyl diphenyl sulfide, ***2l***

Colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.62$ (s, 2H), 7.54 (d, $J = 7.2$ Hz, 2H), 7.51–7.44 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 136.2$, 134.2, 131.4 (q, $^2J_{\mathrm{CF}} = 33.0$ Hz), 129.9, 127.7(q, $^3J_{\mathrm{CF}} = 4.0$ Hz), 124.4 (q, $^3J_{\mathrm{CF}} = 4.0$ Hz), 123.6 (q, $^1J_{\mathrm{CF}} = 271.0$ Hz). Anal. Calcd. for $C_{14}H_8F_6S$: C, 52.18; H, 2.50. Found: C, 52.37; H, 2.31.

2.3.13. 4,4′-Diacetyl diphenyl sulfide, ***2m*** *[40]*

Yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.91$ (dd, $J = 1.6$, 6.8 Hz, 4H), 7.40 (dd, $J = 1.6$, 6.8 Hz, 4H), 2.61 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 197.1$, 141.1, 135.9, 130.6, 129.3, 26.6.

2.3.14. Bis(3-pyridyl) sulfide ***2n*** *[40]*

Colorless oil. ^{1}H NMR(CDCl$_3$, 400 MHz): $\delta = 8.61$ (s, 2H), 8.54–8.52 (m, 2H), 7.67–7.65 (m, 2H), 7.29–7.25 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 151.7$, 148.7, 138.7, 131.9, 124.2.

2.3.15. Bis(1-naphthyl) sulfide ***2o*** *[62]*

White solid. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.36$–8.33 (m, 2H), 7.83–7.80 (m, 2H), 7.72–7.70 (m, 2H), 7.48–7.45 (m, 4H), 7.25–7.18 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 134.1$, 132.6, 132.4, 129.9, 128.6, 128.0, 126.8, 126.4, 125.9, 125.1.

3. Results and discussion

3.1. Synthesis and characterization of MCM-41-2N–CuCl

The MCM-41-immobilized bidentate nitrogen/CuCl complex (MCM-41-2N–CuCl) was very conveniently prepared starting from commercially available and inexpensive 3-(2-aminoethylamino)propyltrimethoxysilane and CuCl (Scheme 1). Firstly, the mesoporous material MCM-41 reacted with 3-(2-aminoethylamino)propyltrimethoxysilane in toluene at 100 °C for 24 h to generate 3-(2-aminoethylamino)propyl-functionalized MCM-41 (MCM-41-2N). The latter was subsequently treated with CuCl in DMF at room temperature for 7 h to generate the MCM-41-immobilized bidentate nitrogen/CuCl complex (MCM-41-2N–CuCl) as a pale blue powder, the copper content of the complex was found to be 0.46 mmol/g according to the ICP-AES measurements. XRD patterns of the parent MCM-41 and the modified materials MCM-41-2N, MCM-41-2N–CuCl are displayed in Fig. 1. Small angle X-ray powder diffraction of the parent MCM-41 gave peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2N and MCM-41-2N–CuCl, the (100) reflection of the parent MCM-41 with decreased intensity was remained after functionalization, while the (110) and (200) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41

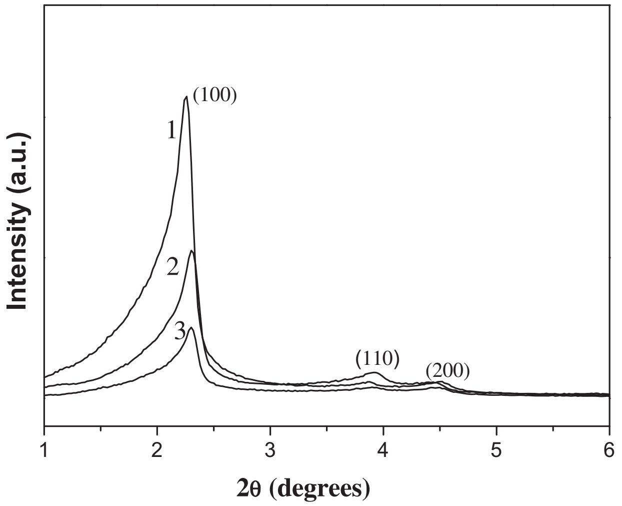
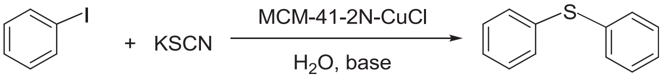


Fig. 1. XRD profiles of the parent MCM-41 (1), MCM-41-2N (2) and MCM-41-2N–CuCl (3).

Table 1
Reaction condition screening for the coupling of iodobenzene with KSCN.[a]



Entry	Base	Temp (°C)	Time (h)	Yield[b] (%)
1	Na_2CO_3	130	48	47
2	K_2CO_3	130	48	59
3	Cs_2CO_3	130	48	88
4	$KHCO_3$	130	48	42
5	K_3PO_4	130	48	50
6	NaOAc	130	48	68
7	Et_3N	130	48	60
8	Bu_3N	130	48	66
9	Piperidine	130	48	69
10	Pyridine	130	48	54
11	DBU	130	48	61
12	Cs_2CO_3	120	60	81
13	Cs_2CO_3	100	72	65
14	Cs_2CO_3	140	48	86
15	Cs_2CO_3	130	24	71
16	Cs_2CO_3	130	60	86
17[c]	Cs_2CO_3	130	72	65
18[d]	Cs_2CO_3	130	30	87
19[e]	Cs_2CO_3	130	48	89
20[f]	Cs_2CO_3	130	48	61
21[g]	Cs_2CO_3	130	48	72

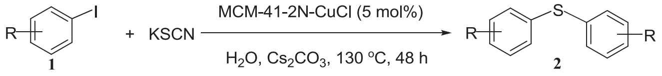
[a] Reaction conditions: iodobenzene (1.0 mmol), KSCN (1.5 mmol), copper catalyst (110 mg, 0.05 mmol), base (2.0 mmol), H_2O (3.0 mL) under Ar.
[b] Isolated yield.
[c] Copper catalyst (55 mg, 0.025 mmol) was used.
[d] Copper catalyst (220 mg, 0.1 mmol) was used.
[e] $(n\text{-Bu})_4NF$ (0.2 mmol) was used as a PTC.
[f] MCM-41-2N–CuBr (117 mg, 0.05 mmol) was used.
[g] MCM-41-2N–CuI (102 mg, 0.05 mmol) was used.

[61,63]. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

3.2. Heterogeneous C–S coupling reactions of aryl iodides with potassium thiocyanate

In our initial screening experiments, iodobenzene and potassium thiocyanate were selected as model substrates to optimize the reaction conditions, and the results are summarized in Table 1. At first, the base effect was examined, and a significant base effect was observed. It is evident that good yields were obtained when Cs_2CO_3, NaOAc, piperidine and Bu_3N were used as the base (Table 1, entries 3, 6, 8 and 9), whereas Na_2CO_3, K_2CO_3, $KHCO_3$, K_3PO_4, Et_3N, pyridine, and DBU afforded low to moderate yields (Table 1, entries 1, 2, 4, 5, 7, 10, 11), so Cs_2CO_3 was finally selected as the base for the reaction. Our next studies focused on the effect of reaction temperature and time on the model reaction. For the temperatures tested [100, 120, 130, and 140 °C], 130 °C gave the best result. It was found that the reaction was accomplished when it was carried out in water at 130 °C for 48 h. Finally, the amount of supported copper catalyst was also screened, and 5.0 mol% loading of copper was found to be optimal, a lower yield was observed when the amount of the catalyst was decreased (Table 1, entry 17). Increasing the amount of copper catalyst could shorten the reaction time, but did not increase the yield of diphenyl sulfide (Table 1, entry 18). The addition of $(n\text{-Bu})_4NF$ (0.2 equiv) as a PTC also did not enhance the yield (Table 1, entry 19). To verify the effect of the anion of copper(I) salts on the reaction, we also prepared MCM-41-2N–CuBr and MCM-41-2N–CuI from CuBr or CuI instead of CuCl according to Scheme 1. It was found that lower yields were obtained when MCM-41-2N–CuBr or MCM-41-2N–CuI was used as the catalyst (Table 1, entries 20 and 21). Therefore, the optimal catalytic system involved the use of MCM-41-2N–CuCl (5 mol%), Cs_2CO_3 (2 equiv) in neat water at 130 °C under Ar for 48 h (Table 1, entry 3).

Table 2
Heterogeneous copper-catalyzed C–S coupling of different aryl iodides with potassium thiocyanate.[a]



Entry	Ar/I	Product	Yield[b] (%)
1	Ph/I	**2a**	88
2	$4\text{-}CH_3C_6H_4/I$	**2b**	86
3	$2\text{-}CH_3C_6H_4/I$	**2c**	75
4	$4\text{-}CH_3OC_6H_4/I$	**2d**	78
5	$2\text{-}CH_3OC_6H_4/I$	**2e**	69
6	$3\text{-}CH_3OC_6H_4/I$	**2f**	84
7	$4\text{-}ClC_6H_4/I$	**2g**	82
8	$4\text{-}BrC_6H_4/I$	**2h**	81
9	$4\text{-}FC_6H_4/I$	**2i**	85
10	$4\text{-}O_2NC_6H_4/I$	**2j**	83
11	$2\text{-}O_2NC_6H_4/I$	**2k**	70
12	$3\text{-}CF_3C_6H_4/I$	**2l**	86
13	$4\text{-}CH_3COC_6H_4/I$	**2m**	84
14	3-Pyridinyl/I	**2n**	61
15	1-Naphthyl/I	**2o**	65

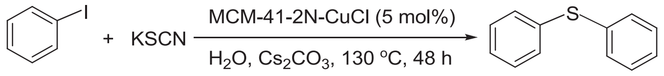
[a] Reaction conditions: aryl iodide (1.0 mmol), KSCN (1.5 mmol), MCM-41-2N–CuCl (110 mg, 0.05 mmol), Cs_2CO_3 (2.0 mmol), H_2O (3.0 mL) at 130 °C under Ar for 48 h.
[b] Isolated yield.

Then, a variety of aryl iodides were examined to explore the scope of substrates under the optimized reaction conditions and the results are listed in Table 2. As shown in Table 2, the C–S coupling reactions of a variety of aryl iodides with KSCN proceeded smoothly to afford the corresponding diaryl sulfides in moderate to high yields. The electron nature of substituents seemed to have no effect on the results, various electron-donating and electron-withdrawing substituents such as $-CH_3$, $-OCH_3$, –Br, –Cl, –F, $-CF_3$, $-COCH_3$ and $-NO_2$ on aryl iodides were well tolerated. The reactions of sterically hindered aryl iodides such as 2-iodotoluene, 2-iodoanisole, and 2-nitroiodobenzene with potassium thiocyanate also provided good yields of the desired diaryl sulfides **2c**, **2e** and **2k** under the optimized reaction conditions, respectively (Table 2, entries 3, 5 and 11), although the effect of steric hindrance on the reaction was observed. Moreover, high yields obtained in the case of 4-chloroiodobenzene, 4-bromoiodobenzene and 4-fluoroiodobenzene indicated that there was good chemoselectivity between iodide, bromide, chloride, and fluoride functional groups (Table 2, entries 7–9). A heteroaryl iodide, such as 3-iodopyridine, could also afford the desired diaryl sulfide **2n** in 61% yield (Table 2, entry 14). The bulky 1-iodonaphthalene also reacted effectively with KSCN to give the corresponding product **2o** in 65% yield (Table 2, entry 15). The method provides a quite general route for the synthesis of diaryl sulfides having various functionalities. The results above prompted us to investigate the reaction of aryl bromides with KSCN. However, aryl bromides were not reactive under the optimized reaction conditions for aryl iodides and no desired product was obtained.

3.3. Recycling of the catalyst

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability and reusability.

Table 3
The C–S coupling reaction of iodobenzene with KSCN catalyzed by the recycled catalyst.[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	88	2	88
3	87	4	86
5	87	6	87
7	86	8	85
9	86	10	85

[a] Reaction was carried out with iodobenzene (1 mmol), KSCN (1.5 mmol), MCM-41-2N–CuCl (110 mg, 0.05 mmol), Cs_2CO_3 (2.0 mmol), H_2O (3.0 mL) at 130 °C under Ar for 48 h.

[b] Isolated yield.

We also investigated the recyclability of the MCM-41-2N–CuCl by using the C–S coupling reaction of iodobenzene with KSCN. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, ethyl acetate and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was used in the next run, and almost consistent activity was observed for 10 consecutive cycles (Table 3, entries 1–10). Fig. 2 shows the time course of the coupling reaction of iodobenzene with KSCN using the fresh and the tenth recycled catalysts. As shown in Fig. 2, for the tenth recycled catalyst, the induction period and the reaction rate in the tenth run did not change significantly compared with that of the fresh one, indicating that the catalytic system is robust for this coupling reaction. In addition, copper leaching in the immobilized catalyst was also determined. The copper content of the catalyst was found by ICP analysis to be 0.45 mmol/g after ten consecutive runs, only 2% of copper had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst may result from the chelating action of bidentate 2-aminoethylamino ligand on copper and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2N–CuCl make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

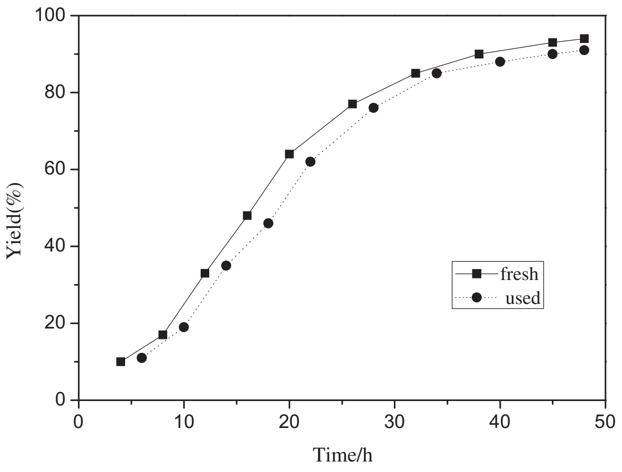


Fig. 2. Plot of GC yield versus time for the coupling reaction of iodobenzene with KSCN using the fresh and the tenth recycled catalysts.

4. Conclusion

In summary, we have developed a novel, practical and environmentally friendly access to diaryl sulfides through the reaction of aryl iodides with KSCN by using an MCM-41-immobilized bidentate nitrogen/CuCl complex [MCM-41-2N–CuCl] as catalyst in neat water. One of the advantages derived from the use of such a benign solvent as water are clear in terms of safety, cost and innocuousness. Furthermore, the methodology is applicable to a variety of aryl iodides. This heterogeneous copper catalyst can be very conveniently prepared by a simple two-step procedure from commercially available and cheap reagents. In addition, this methodology offers the competitiveness of recyclability of the catalyst without significant loss of catalytic activity, and the catalyst could be easily recovered and reused for at least 10 cycles, providing thereby environmental and economic advantages over previously reported protocols and rendering this methodology highly suitable for industrial application.

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