

Accepted Manuscript

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PII: S1381-1169(14)00357-4
DOI: <http://dx.doi.org/doi:10.1016/j.molcata.2014.08.010>
Reference: MOLCAA 9225

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 16-12-2013
Revised date: 4-8-2014
Accepted date: 5-8-2014

Please cite this article as: M. Cai, R. Yao, L. Chen, H. Zhao, A simple, efficient and recyclable catalytic system for carbon-sulfur coupling of aryl halides with thioacetamide, *Journal of Molecular Catalysis A: Chemical* (2014), <http://dx.doi.org/10.1016/j.molcata.2014.08.010>

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A simple, efficient and recyclable catalytic system for carbon-sulfur coupling of aryl halides with thioacetamide

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Research Highlights

- ▶ The MCM-41-2N-CuI complex could be conveniently prepared by a simple procedure.
- ▶ This heterogeneous copper catalyst exhibited higher catalytic activity than CuI.
- ▶ This copper catalyst can be reused for 10 times without any decrease in activity.
- ▶ Our catalytic system provides a practical route for the synthesis of diaryl sulfides.

Abstract

The carbon-sulfur coupling reaction of aryl halides with thioacetamide using an MCM-41-immobilized bidentate nitrogen copper(I) complex [MCM-41-2N-CuI] as an efficient heterogeneous catalyst is described. Developed catalytic system is found

to be effective for the coupling reaction of aryl halides with thioacetamide providing moderate to high yield of diaryl sulfides. This heterogeneous copper catalyst exhibits higher activity than CuI and can be recovered by a simple filtration of the reaction solution and reused for at least 10 consecutive trials without any decreases in activity.

Keywords: Supported copper catalyst; Carbon-sulfur coupling; Functionalized MCM-41; Diaryl sulfide; Aryl halide

1. Introduction

The aryl-sulfur bonds proverbially exist in a great number of pharmaceuticals, biologically active molecules and polymeric materials [1-6]. 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 [7,8]. However, the related C-S bond, which is to bind to metals, acting as metal deactivators [9]. Traditional methods for the construction 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 [10]. Reduction of aryl sulfones or aryl sulfoxides requires strong reducing agents such as DIBAL-H or LiAlH₄ [11-13]. The development of efficient methods for the formation of aryl-sulfur bonds has been a subject of interest in synthetic chemistry since Migita *et al.* first reported cross-coupling reactions of aryl halides with thiols in the presence of a palladium catalyst [14,15]. A wide range of transition metals were used to catalyze this coupling reaction, including palladium

[16-21], nickel [22,23], cobalt [24], copper [25-31], and indium [32,33]. Among these methods, the copper-catalyzed cross-coupling is highly attractive due to the relatively low cost and environmentally negative influence of the process [34].

On the other hand, the common methods for the synthesis of diaryl sulfides are based on the condensation of aryl halides with thiols, however, the use of volatile and foul-smelling thiols has been a main drawback, which may bring about safety problems. In addition, some thiols are too expensive for scale-up operations. In the meantime, Still and Toste reported that diaryl sulfides could be prepared via the reaction of samarium thiolates with aryl halides [35]. Firouzabadi *et al.* described thioetherification of aryl halides using thiourea as a nonvolatile sulfur source [36]. The copper-catalyzed synthesis of diaryl sulfides from aryl halides with potassium thiocyanate or thioacetamide has also been reported [31,37]. Although these copper-catalyzed formation reactions of aryl-sulfur bonds are highly efficient, the problem with homogeneous catalysis is the difficulty to separate the 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 isolated product, which is a particularly significant drawback for its application in the pharmaceutical industry. To overcome these problems, the development of highly active and recyclable heterogeneous catalysts, such as immobilization of catalytically active species, *i.e.* organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst is essential [38,39]. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the

development of green chemical processes [40,41]. In spite of tremendous effort dedicated to the immobilization of homogeneous palladium complexes over the last two decades [42-44], very few examples of carbon-carbon or carbon-heteroatom bond formation reactions catalyzed by heterogeneous copper catalysts have appeared [45-48]. Therefore, the development of a stable heterogeneous copper catalyst that allows for highly efficient thioetherification 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 $> 700 \text{ m}^2 \text{ g}^{-1}$ [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 [39,54-57]. However, to the best of our knowledge, no the synthesis of diaryl sulfides 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, our new approach, described in this paper, was to design and synthesize an MCM-41-immobilized bidentate nitrogen copper(I) complex (MCM-41-2N-CuI), which was used as an effective copper catalyst for the carbon-sulfur coupling reaction of aryl halides with thioacetamide.

2. Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [58]. All reactions were performed under an inert atmosphere of argon using distilled solvents. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^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 patterns were obtained on Damx-rA (Rigaku).

2.1. Preparation of MCM-41-2N

A solution of 1.54 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. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 ml of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3×20 ml) and diethyl ether (3×20 ml), and dried in vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol/g by elemental analysis.

2.2. Preparation of MCM-41-2N-CuI

In a small Schlenk tube, 1.0 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.1 g (0.52 mmol) of CuI 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 40 °C/26.7 Pa under Ar for 5 h to give 1.066 g of a pale blue copper complex (MCM-41-2N-CuI). The nitrogen and copper content was found to be 1.67 mmol g⁻¹ and 0.45 mmol g⁻¹, respectively.

2.3. General procedure for the coupling of aryl halides with thioacetamide

A Schlenk tube was charged with MCM-41-2N-CuI (66 mg, 0.03 mmol), MeCSNH₂ (75 mg, 1.0 mmol), Cs₂CO₃ (978 mg, 3.0 mmol), and aryl halide (2.5 mmol). The tube was evacuated and backfilled with argon. Then, DMSO-H₂O (1 ml/0.5 ml) was added under argon. The tube was sealed, and the reaction mixture was stirred at 120 °C for 24-48 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 ml), and filtered. The MCM-41-2N-CuI complex was washed with distilled water (2 × 5 ml), ethanol (2 × 5 ml), and Et₂O (2 × 5 ml) and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate = 50:1 to 7:1) to provide the desired product.

3. Results and discussion

An MCM-41-immobilized bidentate nitrogen copper(I) complex (MCM-41-2N-CuI) was conveniently prepared from commercially available and inexpensive 3-(2-amino-

ethylamino)propyltrimethoxysilane and CuI (Scheme 1). Firstly, the mesoporous material MCM-41 reacted with 3-(2-aminoethylamino)propyltrimethoxysilane in toluene at 100 °C for 24 h, followed by the silylation with Me₃SiCl in toluene at room temperature for 24 h to give 3-(2-aminoethylamino)propyl-functionalized MCM-41 (MCM-41-2N). The latter was subsequently treated with CuI in DMF at room temperature for 7 h to generate the MCM-41-immobilized bidentate nitrogen copper(I) complex (MCM-41-2N-CuI) as a pale blue powder, the copper content of the complex was found to be 0.45 mmol g⁻¹ according to the ICP-AES measurements. X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-2N-CuI are displayed in Figure 1. Small angle X-ray powder diffraction of the parent MCM-41 gave the peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2N-CuI, 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. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

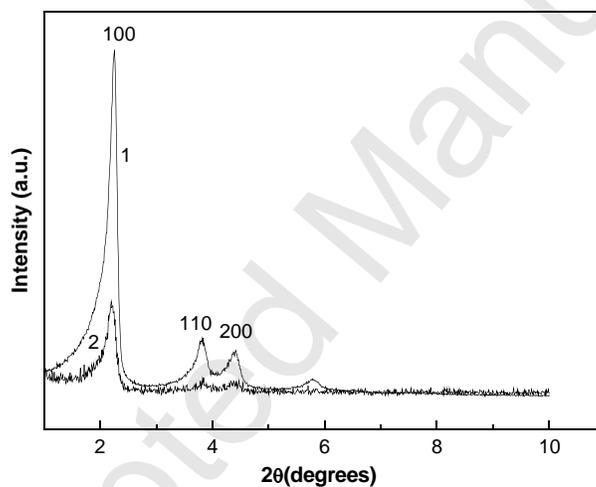
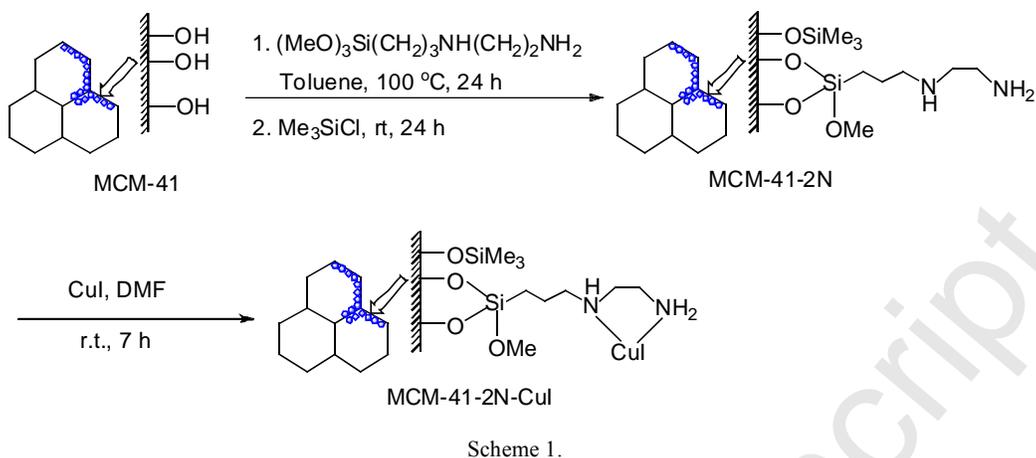
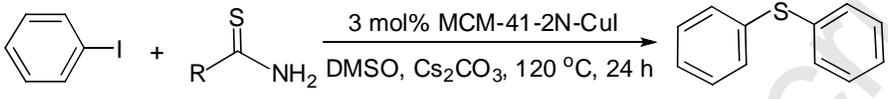


Fig. 1. XRD patterns of the parent MCM-41 (1) and MCM-41-2N-CuI (2)

We started our investigation with iodobenzene as the model substrate to screen the sulfur source using MCM-41-2N-CuI as a catalyst and DMSO as a solvent, and the results are listed in Table 1. When thiourea was used as the sulfur source for synthesis of diphenyl sulfide, the desired product was obtained in 65% yield (entry 1). Substituted thioureas such as amidothiourea gave poor result (entry 2). We were delighted to find that the coupling reaction of iodobenzene with thioacetamide

afforded diphenyl sulfide in 84% yield (entry 3). However, the reaction of iodobenzene with benzothiourea gave diphenyl sulfide in moderate yield (entry 4).

Table 1 Cross-coupling of iodobenzene with various sulfur sources catalyzed by MCM-41-2N-CuI^a



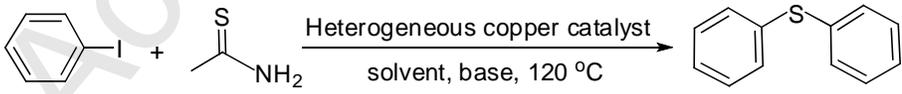
Entry	R	Yield ^b (%)	Entry	R	Yield ^b (%)
1	H ₂ N	65	2	H ₂ NNH	11
3	Me	84	4	Ph	57

^a All reactions were performed using 2.5 mmol of iodobenzene, 1.0 mmol of sulfur source, 3.0 mmol of Cs₂CO₃ and 3 mol% MCM-41-2N-CuI in 1.5 ml of DMSO at 120 °C for 24 h under Ar. ^b Isolated yield based on the sulfur source used.

Subsequently, we chose the cross-coupling of iodobenzene with thioacetamide as model reaction to screen the solvents, bases, and catalyst quantity and the results are outlined in Table 2. First, using MCM-41-2N-CuI as a catalyst, different solvents were examined (entries 1-7). Among the solvents examined [DMSO, DMF, THF, dioxane, and H₂O], DMSO was found to be the most effective (entry 1), DMF afforded moderate yield (entry 2). While no desired product was formed when other solvents such as THF, dioxane, and H₂O were used (entries 3-5). To our delight, slightly increased yields were observed when mixed solvents such as DMSO-H₂O and DMF-H₂O were used (entries 6 and 7). The slightly increased yields may be explained by the fact that the hydrolysis reaction of the reaction intermediate can be accelerated due to the introduction of H₂O. Next, the influence of different bases on the reaction

was tested. Although good yields were also obtained when Na_2CO_3 , K_2CO_3 , and K_3PO_4 were used as the base (entries 8-10), Cs_2CO_3 gave the best result (entry 6). 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-CuCl from CuBr or CuCl instead of CuI according to Scheme 1. It was found that lower yields were obtained when MCM-41-2N-CuBr or MCM-41-2N-CuCl was used as the catalyst (entries 11 and 12). Finally, the amount of supported copper catalyst was also screened, and 3.0 mol% loading of copper was found to be optimal, a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (entries 15 and 16). Increasing the amount of copper catalyst could shorten the reaction time, but did not increase the yield of diphenyl sulfide (entries 13 and 14). Thus, the optimized reaction conditions for this cross-coupling of iodobenzene with thioacetamide are the MCM-41-2N-CuI (3 mol%) in DMSO- H_2O (2:1) using Cs_2CO_3 as base at 120 °C under Ar for 24 h (entry 6).

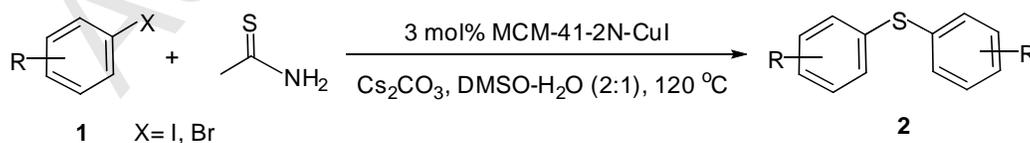
Table 2 Cross-coupling reaction of iodobenzene with thioacetamide in different conditions^a



Entry	Catalyst (mol%)	Solvent (2:1)	Base	Time (h)	Yield ^b (%)
1	MCM-41-2N-CuI (3)	DMSO	Cs_2CO_3	24	84
2	MCM-41-2N-CuI (3)	DMF	Cs_2CO_3	24	58
3	MCM-41-2N-CuI (3)	THF	Cs_2CO_3	36	0

4	MCM-41-2N-CuI (3)	Dioxane	Cs ₂ CO ₃	36	0
5	MCM-41-2N-CuI (3)	H ₂ O	Cs ₂ CO ₃	36	0
6	MCM-41-2N-CuI (3)	DMSO-H ₂ O	Cs ₂ CO ₃	24	88
7	MCM-41-2N-CuI (3)	DMF-H ₂ O	Cs ₂ CO ₃	24	63
8	MCM-41-2N-CuI (3)	DMSO-H ₂ O	K ₂ CO ₃	24	72
9	MCM-41-2N-CuI (3)	DMSO-H ₂ O	Na ₂ CO ₃	24	67
10	MCM-41-2N-CuI (3)	DMSO-H ₂ O	K ₃ PO ₄	24	75
11	MCM-41-2N-CuBr (3)	DMSO-H ₂ O	Cs ₂ CO ₃	24	72
12	MCM-41-2N-CuCl (3)	DMSO-H ₂ O	Cs ₂ CO ₃	24	74
13	MCM-41-2N-CuI (5)	DMSO-H ₂ O	Cs ₂ CO ₃	18	87
14	MCM-41-2N-CuI (10)	DMSO-H ₂ O	Cs ₂ CO ₃	10	88
15	MCM-41-2N-CuI (2)	DMSO-H ₂ O	Cs ₂ CO ₃	48	81
16	MCM-41-2N-CuI (1)	DMSO-H ₂ O	Cs ₂ CO ₃	72	76

^aAll reactions were performed using 2.5 mmol of iodobenzene, 1.0 mmol of thioacetamide, 3.0 mmol of base in 1.5 ml of solvent at 120 °C under Ar. ^b Isolated yield based on thioacetamide used.



Scheme 2.

To examine the scope for this heterogeneous copper-catalyzed coupling reaction, we have investigated the reactions using a variety of aryl iodides or bromides as the

substrates under the optimized reaction conditions (Scheme 2) and the results are summarized in Table 3. As shown in Table 3, the C–S coupling reactions of a variety of aryl iodides with thioacetamide proceeded smoothly to afford the corresponding diaryl sulfides in good to excellent yields. The electron nature of substituents seemed to have no effect on the results, various electron-donating and electron-withdrawing substituents such as $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{Br}$, $-\text{Cl}$, $-\text{F}$, $-\text{CF}_3$, $-\text{CN}$, $-\text{COCH}_3$ and $-\text{NO}_2$ on aryl iodide were well tolerated. This heterogeneous copper catalyst exhibited higher activity than homogeneous CuI. For instance, in the presence of 3 mol% MCM-41-2N-CuI, the reactions of iodobenzene and 4-iodoanisole with thioacetamide in DMSO-H₂O (2:1) with Cs₂CO₃ as base at 120 °C under Ar for 24 h afforded 88% yield of **2a** and 93% yield of **2d**, respectively (entries 1 and 4). The same reactions in the presence of 10 mol% CuI in DMSO-H₂O (2:1) with Cs₂CO₃ as base at 120 °C under Ar for 24 h gave 83% yield of **2a** and 87% yield of **2d**, respectively [37]. The higher activity of MCM-41-2N-CuI over CuI may be explained by the fact that the chemical bonding between metal complexes and functional groups of the support maintains the isolated nature of metal complexes, which can influence the catalytic performance in a manner that the analogous homogeneous complex does not exhibit in solution [59]. Aryl iodides carrying an *ortho* substituent were also found to readily participate in the reaction. For example, the reactions of 2-iodotoluene, 2-iodoanisole, and 2-iodoaniline with thioacetamide provided good yields of the desired diaryl sulfides **2c**, **2e** and **2o** under the optimized reaction conditions, respectively (entries 3, 5 and 15), although the effect of steric hindrance on the reaction was observed.

Moreover, good yields obtained in the case of 4-chloriodobenzene, 4-bromoiodobenzene and 4-fluoriodobenzene indicated that there was good chemoselectivity between iodide, bromide, chloride, and fluoride functional groups (entries 6, 10 and 11). A heteroaryl iodide, such as 3-iodopyridine, could afford the desired diaryl sulfide **2q** in 74% yield (entry 17). The bulky 1-iodonaphthalene also reacted effectively with thioacetamide to give the corresponding product **2p** in 82% yield (entry 16). 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 thioacetamide. The reactivity of aryl bromides was obviously lower than that of aryl iodides. It was found that nonactivated aryl bromides such as bromobenzene and 4-bromotoluene were not reactive under the present reaction conditions (entries 23 and 24). However, the reactions of electron-deficient aryl bromides with thioacetamide could proceed to give moderate to good yields (40-79%) of diaryl sulfides (entries 18-22).

Table 3 Heterogeneous copper-catalyzed cross-coupling of aryl iodides or bromides with thioacetamide^a

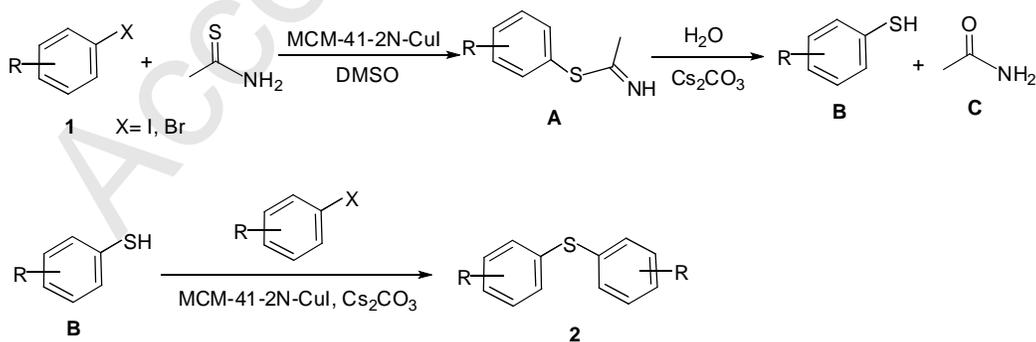
Entry	Ar	X	Time (h)	Product	Yield ^b (%)
1	Ph	I	24	2a	88
2	4-MeC ₆ H ₄	I	24	2b	89
3	2-MeC ₆ H ₄	I	30	2c	85
4	4-MeOC ₆ H ₄	I	24	2d	93
5	2-MeOC ₆ H ₄	I	30	2e	72
6	4-FC ₆ H ₄	I	24	2f	81
7	3-CF ₃ C ₆ H ₄	I	24	2g	78

8	3-MeC ₆ H ₄	I	24	2h	86
9	4-O ₂ NC ₆ H ₄	I	24	2i	89
10	4-ClC ₆ H ₄	I	24	2j	79
11	4-BrC ₆ H ₄	I	24	2k	76
12	4-MeCOC ₆ H ₄	I	24	2l	70
13 ^c	4-CNC ₆ H ₄	I	24	2m	68
14	3-O ₂ NC ₆ H ₄	I	24	2n	85
15	2-H ₂ NC ₆ H ₄	I	30	2o	84
16	1-naphthyl	I	24	2p	82
17	3-pyridinyl	I	24	2q	74
18	4-ClC ₆ H ₄	Br	36	2j	59
19	4-MeCOC ₆ H ₄	Br	36	2l	76
20	4-O ₂ NC ₆ H ₄	Br	36	2i	79
21 ^c	4-CNC ₆ H ₄	Br	36	2m	51
22	2-pyridinyl	Br	36	2r	45
23	Ph	Br	48	2a	Trace
24	4-MeC ₆ H ₄	Br	48	2b	0

^a All reactions were performed using 2.5 mmol of aryl halide, 1.0 mmol of thioacetamide, 3.0 mmol of Cs₂CO₃ and 3 mol% of MCM-41-2N-CuI in DMSO-H₂O (1.0 ml/0.5 ml) at 120 °C under Ar. ^b Isolated yield based on thioacetamide used. ^c Solvent: DMSO (1.5 ml).

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2N-CuI or to a leached copper species in solution, we performed the hot filtration test [60]. We focused on the cross-coupling reaction of iodobenzene with thioacetamide. We filtered off the MCM-41-2N-CuI complex after 10 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (120 °C) in order to avoid possible recoordination or

precipitation of soluble copper upon cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached copper species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no copper could be detected in the hot filtered solution. This result suggests that the copper catalyst remains on the support at elevated temperature during the reaction. Although the detailed mechanistic studies of copper-catalyzed couplings of thiols are lacking in the literature, this heterogeneous copper-catalyzed cross-coupling reaction of aryl halides with thioacetamide may proceed through a mechanism analogous to that proposed for CuI (Scheme 3) [37]. First, the coupling reaction of aryl halide (**1**) with thioacetamide in the presence of MCM-41-2N-CuI provides aryl ethanimidothioate (**A**), which is hydrolyzed in the reaction mixture to afford a thiol (**B**) along with acetamide as a side product (**C**) under the basic conditions. Then the newly generated arylthiol intermediate (**B**) reacts with aryl halide (**1**) under the same catalytic system to give the diaryl sulfide (**2**).

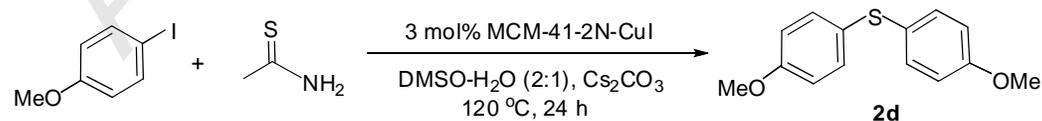


Scheme 3.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of

separation, recoverability and reusability. We also investigated the recyclability of the MCM-41-2N-CuI by using the coupling reaction of 4-iodoanisole with thioacetamide. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, ethanol 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 4, entries 1-10). In addition, copper leaching in the immobilized catalyst was also determined. The copper content of the catalyst was found by ICP analysis to be 0.44 mmol g⁻¹ 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 should 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-CuI make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Table 4 Cross-coupling reaction of 4-iodoanisole with thioacetamide catalyzed by the recycled catalyst^a



Cycle	Yield ^b (%)	Cycle	Yield ^b (%)
1	93	2	92
3	92	4	93
5	91	6	92

7	91	8	90
9	91	10	90

^a Reaction was carried out with 4-iodoanisole (2.5 mmol), thioacetamide (1.0 mmol), MCM-41-2N-CuI (0.03 mmol), Cs₂CO₃ (3.0 mmol), DMSO-H₂O (1.0 ml/0.5 ml) at 120 °C under Ar for 24 h. ^b Isolated yield.

4. Conclusion

In summary, we have developed a novel, practical and environmentally friendly catalyst system for the coupling reaction of aryl halides with thioacetamide by using an MCM-41-immobilized bidentate nitrogen copper(I) complex [MCM-41-2N-CuI] as catalyst. This novel heterogeneous copper catalyst can be conveniently prepared by a simple two-step procedure from commercially available and inexpensive reagents and exhibits higher catalytic activity than CuI. The reactions generated a variety of diaryl sulfides in moderate to high yields and were applicable to various aryl iodides and bromides. In addition, this methodology offers the competitiveness of recyclability of the catalyst without significant loss of catalytic activity, and the catalyst can be readily recovered by a simple filtration and reused for 10 cycles, thus making this procedure environmentally more acceptable.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21272044) and Scientific Research Fund of Education Department of Jiangxi Province (KJLD13022) for financial support.

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Captions

1. Scheme 1: Preparation of the MCM-41-2N-CuI
2. Figure 1: XRD patterns of the parent MCM-41 (1) and MCM-41-2N-CuI (2)
3. Table 1: Cross-coupling of iodobenzene with various sulfur sources catalyzed

by MCM-41-2N-CuI

4. Table 2: Cross-coupling reaction of iodobenzene with thioacetamide in different conditions
5. Scheme 2: Cross-coupling of aryl halides with thioacetamide catalyzed by MCM-41-2N-CuI
6. Table 3: Heterogeneous copper-catalyzed cross-coupling of aryl iodides or bromides with thioacetamide
7. Scheme 3: Possible mechanism for heterogeneous copper-catalyzed coupling of aryl halides with thioacetamide
8. Table 4: Cross-coupling reaction of 4-iodoanisole with thioacetamide catalyzed by the recycled catalyst

Graphical Abstract

A simple, efficient and recyclable catalytic system for carbon-sulfur coupling of aryl halides with thioacetamide

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