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Highly efficient and reusable polystyrene-supported copper(II) catalytic system for S-arylation of potassium thiocyanate by aryl halides in water

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An inexpensive, efficient and environmentally friendly copper(II) catalyst supported on polystyrene was successfully synthesized and used as a heterogeneous catalyst for S-arylation of potassium thiocyanate by aryl halides. Also this catalyst could be recovered and reused several times without any noticeable decrease in its catalytic activity. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: copper(II) catalyst; C–S coupling; symmetric diaryl sulfides; heterogeneous catalyst; aryl halides

Introduction

The making of carbon–sulfur bonds is a significant instrument in organic synthesis, because of broad applications of organo-sulfur compounds in various fields of science.[1–3] Diaryl thioethers and their oxidized forms exist in a large number of polymeric materials, biologically active molecules and pharmaceutical materials, for example in antiasthmatic, antiallergy, antibipolar disorder, antidiabetes, antischizophrenia and anti-HIV agents.[4–10] Therefore, the creation of carbon–sulfur bonds is of much interest and forms a very important part in the preparation of numerous pharmaceutical, biological and chemical molecules.

In conventional techniques, severe and difficult conditions are used for the creation of carbon–sulfur bonds. For example, reduction of aryl sulfoxides or aryl sulfones with powerful reducing agents is one technique for the preparation of sulfides.[11]

In 1985, Migita and co-workers reported the synthesis of aryl sulfides via reaction of thiols and aryl halides using a palladium catalyst.[12] The employment of unstable and costly thiols with very unpleasant odors represents a dangerous and serious problem. Furthermore, sulfur-containing compounds can behave as destroyers of metal catalysts due to their powerful coordinative characteristics, frequently rendering catalytic reactions useless.[13]

Also, some recently developed procedures involve costly ligands, solvents and catalytic systems,[14] long reaction times,[15] metal pollution of final products and inability to recycle the catalysts. These reasons restrict the use of reactions on large scales. Hence, it is necessary to discover new catalytic systems with cheap metals,[16–18] ligands and solvents and with capability for reuse, for the preparation of these very valuable and useful materials.

Recently, substantial developments have been reported in the scope of heterogeneous catalysis for a wide range of organic reactions.[19–21] Generally, heterogeneous catalysts present lower coordinating sites, higher surface area and facile functionalization which account for the high catalytic activity of these catalysts.[22,23] Moreover, heterogeneous catalysis has the benefits of easy product purification, reusability and high activity. Among these heterogeneous catalysts, copper immobilized on polystyrene has appeared as an interesting material because of its numerous uses in organic synthesis.[24]

Also, during the last few years there has been an interest in studies of green chemical systems. Lately, the employment of water as solvent in chemical reactions has attracted much notice because of its nontoxicity, low price and high accessibility compared with other organic solvents.[25,26]

Water as a solvent was used by Carril and co-workers for the preparation of diaryl sulfides from the reaction of thiophenol derivatives with aryl halides catalyzed by a mixture of a 1,2-diamine derivative and a copper salt.[27] Zhou and co-workers reported an extremely impressive procedure for the formation of carbon–sulfur bonds between potassium thiocyanate and aryl halides using $CuCl_2$/1,10-phenanthroline and $(n\text{-Bu})_4NF$ in water, with no recovery and reusability being described for this catalytic system.[14] Hence, the design of a stable, efficient, inexpensive and heterogeneous copper catalyst that permits very proficient carbon–sulfur bond creation reactions of a broad range of aryl halides is useful.

In continuing done efforts to expand green synthetic paths and heterogeneous catalysis for organic reactions,[28–33] herein we report the 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin-supported Cu(II) (PS-tazo-Cu(II)) complex **3**

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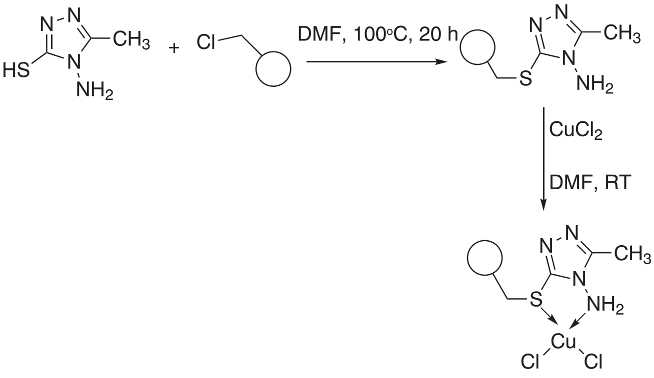


Scheme 1. Synthesis of heterogeneous catalyst PS-tazo-Cu(II) (3).

(Scheme 1), as an inexpensive and efficient catalytic system for the preparation of diaryl sulfides using potassium thiocyanate as the sulfur source in water as solvent.

Results and discussion

4-Amino-5-methyl-3-thio-1,2,4-triazole (**1**) was prepared according to the procedure reported in a literature.[31] The structure of the produced polystyrene-bound triazole (PS-tazo) **2** was characterized using elemental analysis (CHN). The amount of nitrogen of PS-tazo **2** is obtained as 5.6%. Based on this, the amount of triazole attached to the chloromethylated polystyrene is 1 mmol g^{-1} of the polymer. This means that 79.4% of the whole chlorine content is replaced by triazole. Then stirring of polymer-bound triazole **2** with a solution of $CuCl_2{\cdot}5H_2O$ in dimethylformamide (DMF) at room temperature for 6 h (Scheme 1) results in the preparation of PS-tazo-Cu(II) (**3**). The synthesized catalyst **3** was characterized using Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and inductively coupled plasma (ICP) analysis.

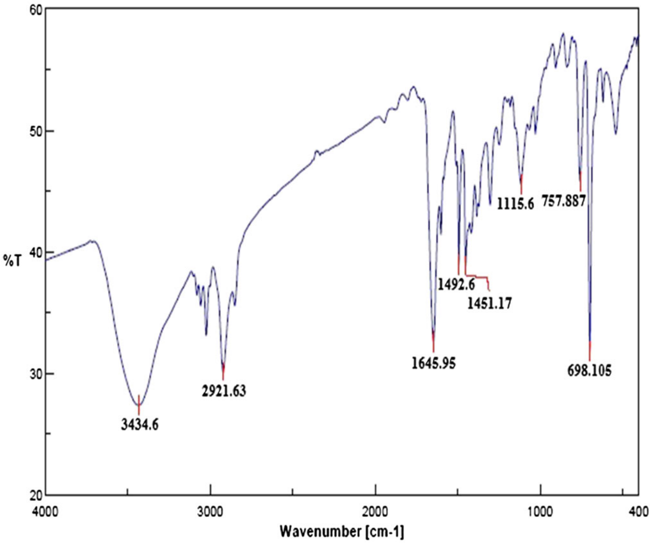


Figure 1. FT-IR spectrum of PS-tazo-Cu(II) complex.

In the FT-IR spectrum of PS-tazo-Cu(II) complex **3** (Fig. 1) can be seen an absorption band at 3434.6 cm^{-1}, which is attributed to the N–H bond. Also the band at 1115.62 cm^{-1} corresponds to the stretching vibrations of the C–N bonds. SEM (Fig. 2) was used to characterize the morphologies of PS-tazo-Cu(II) **3**. As can be seen, the pure polystyrene bead has a flat and smooth surface, while the anchored complex shows coarseness of the top layer. The EDX spectrum (Fig. 3) clearly shows the presence of copper in the synthesized complex. ICP analysis indicates that the amount of copper loaded into the triazole-functionalized polystyrene is 0.46% (0.72 mmol g^{-1}).

To determine the potency of the triazole-functionalized polystyrene resin-supported Cu(II) complex **3**, it was used in the reaction between iodobenzene and potassium thiocyanate in water at 135°C for 7 h (Table 1). First, we examined the effects of bases and additives[24] on this reaction. Among the studied bases, KOH is the best and the corresponding product **6a** is obtained in 95% yield (Table 1, entry 2). Also, among the studied additives, cetyltrimethylammonium bromide (CTAB) is the best (Table 1, entries 2, 5 and 6). Then the effect of temperature was investigated (Table 1, entry 9). As is evident from Table 1, 135°C is the best temperature. Finally, the amount of Cu(II) complex was also studied. A 0.05 mmol loading of Cu(II) is found to be optimal, since a lower yield is obtained when the amount of complex is decreased (Table 1, entry 8).

After we determined the optimized conditions, the PS-triazole-Cu(II) complex **3** was used as a catalyst for the reaction of potassium thiocyanate with aryl halides containing electron-donating or electron-withdrawing substituents. The results obtained are summarized in Table 2. On the whole, all the reactions give corresponding products (Table 2, **6a–6 l**) in good to excellent yields ranging from 55 to 100%. Aryl iodides with electron-withdrawing substituents such as NO_2, Br and Cl (Table 2, entries 2–5) give the corresponding products in higher yields compared with those containing electron-donating groups such as CH_3 and OCH_3 (Table 2, entries 6 and 7). Therefore we these reactions are affected by electronic effects. In addition to aryl iodides, aryl bromides can react with potassium thiocyanate with longer times (Table 2, entries 8–14). Also, aryl chlorides react under these conditions, although their reactivity is lower than that of aryl iodides and bromides (Table 2, entries 15–18).

We propose a mechanism for thioetherification of aryl halides with KSCN as shown in Scheme 2. At first, aryl halide connects to the catalyst and chloride ions leave. In the next step, thiocyanate ion replaces halide ion on the catalyst and an aryl thiocyanate is produced as the first cycle product. Then this product goes into the next cycle and C–S bond is broken in aryl thiocyanate. Second, aryl halide adds to the catalyst and then the product of this cycle (aryl thiocyanate) is obtained through an elimination step and the catalyst enters the next cycle.

Moreover, we investigated the recovery and reusability of the catalyst using the reaction of iodobenzene with potassium thiocyanate as a model system. After completion of this reaction, the copper catalyst from the first run of the reaction was filtered and washed several times with water and ethyl acetate. After drying under vacuum for 6 h, we reused the recovered catalyst in the reaction under the same conditions. As evident from Table 3, the recovered catalyst can be employed successfully for five subsequent runs and exhibits excellent reusability.

To determine the amount of leaching of the copper from the heterogeneous catalyst, after completion of the reaction the catalyst was separated by simple filtration and the copper content of the

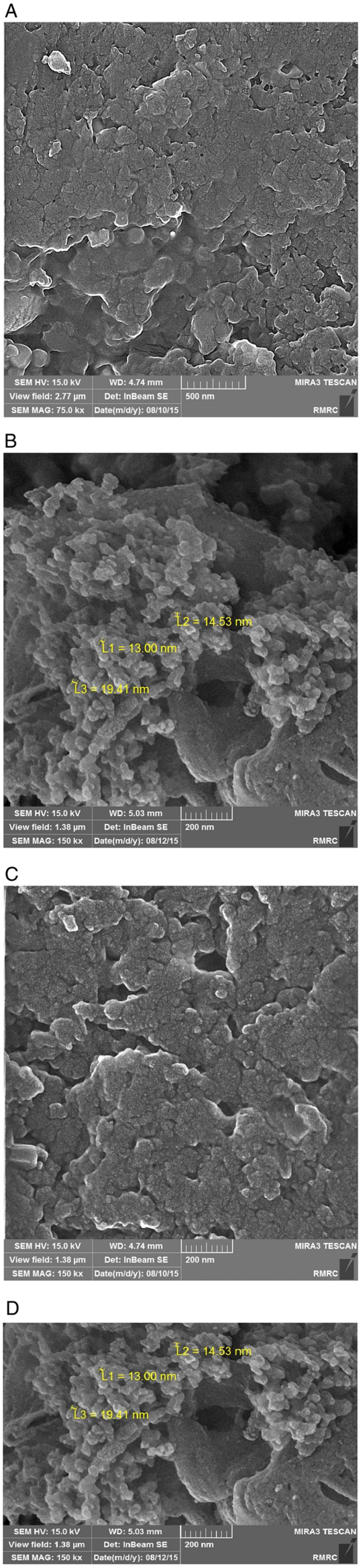


Figure 2. SEM images of chloromethylated polystyrene (A and C) and PS-tazo-Cu(II) complex (B and D).

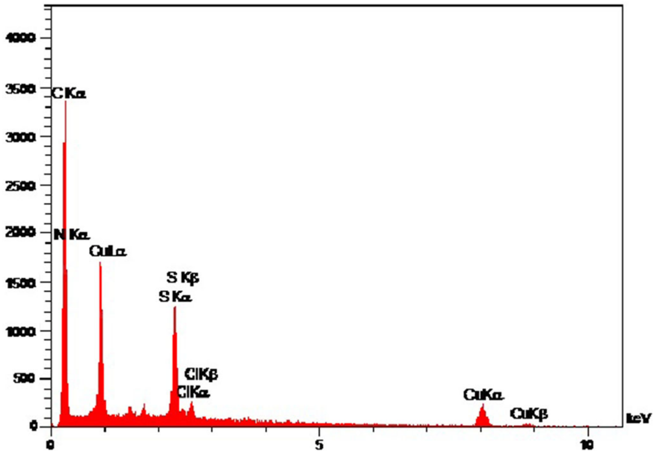


Figure 3. EDX spectrum of polymer-anchored PS-tazo-Cu(II).

filtrate was determined using ICP analysis. It is found that less than 0.15% of the whole amount of the initial copper species is lost into the solution during the reaction. This degree of leaching is unimportant and is confirmed from the excellent reusability of this heterogeneous copper catalyst.

Conclusions

We successfully prepared an inexpensive and efficient polystyrene-supported triazole copper(II) complex, which was employed as a heterogeneous catalyst for the synthesis of diaryl thioethers in water as solvent. The catalyst showed high activity for this reaction within 7 h, and could be easily recovered and reused five times without significant loss in its activity. The high catalytic efficiency, low cost and excellent recyclability means that it is a preferable catalyst compared with the large number of heterogeneous copper catalysts reported to date.

Experimental

General

All chemicals used were of commercial reagent grade and were used without further purification. Chloromethylated polystyrene (4–5% Cl and 2% crosslinked with divinylbenzene) was a product of Merck. The aryl halides and potassium thiocyanate were obtained from Merck or Fluka.

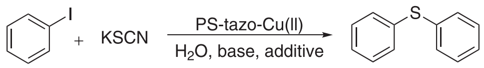
Preparation of polymer-anchored PS-tazo-Cu(II) (3)

The triazole-functionalized polymer **2** was prepared according to the procedure reported in a literature.[31] PS-tazo **2** (1 g) was treated with DMF (20 ml) for 30 min. Then $CuCl_2{\cdot}5H_2O$ (0.2 g) was added, and the resulting mixture was stirred at room temperature for 6 h. The resulting polymer, impregnated with the copper complex, was filtered and washed with ethyl acetate and an ethanol–water mixture and dried at 50°C for 6 h to afford PS-tazo-Cu(II) **3** (Scheme 1).

General procedure for synthesis of diaryl thioethers

A glass flask equipped with a magnetic stirrer was charged with KOH (4.0 mmol), potassium thiocyanate (1.0 mmol), aryl halide

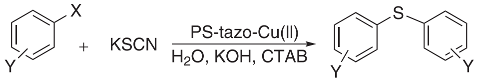
Table 1. Optimization of conditions for reaction of aryl halides and potassium thiocyanate[a]



Entry	Base	Additive	Catalyst (mmol of Cu)	Time (h)	Yield (%)[b]
1	NaOH	CTAB	0.05	7	90
2	KOH	CTAB	0.05	7	95
3	Na_2CO_3	CTAB	0.05	7	80
4	K_2CO_3	CTAB	0.05	7	85
5	KOH	PEG-400[c]	0.05	7	75
6	KOH	TBAB[d]	0.05	7	83
7[e]	KOH	CTAB	0.05	7	72
8	KOH	CTAB	0.04	7	75
9[f]	KOH	CTAB	0.05	7	70
10	KOH	CTAB	0.05	5	72
11	KOH	CTAB	0.05	8	95
12	KOH	CTAB	0.06	7	95

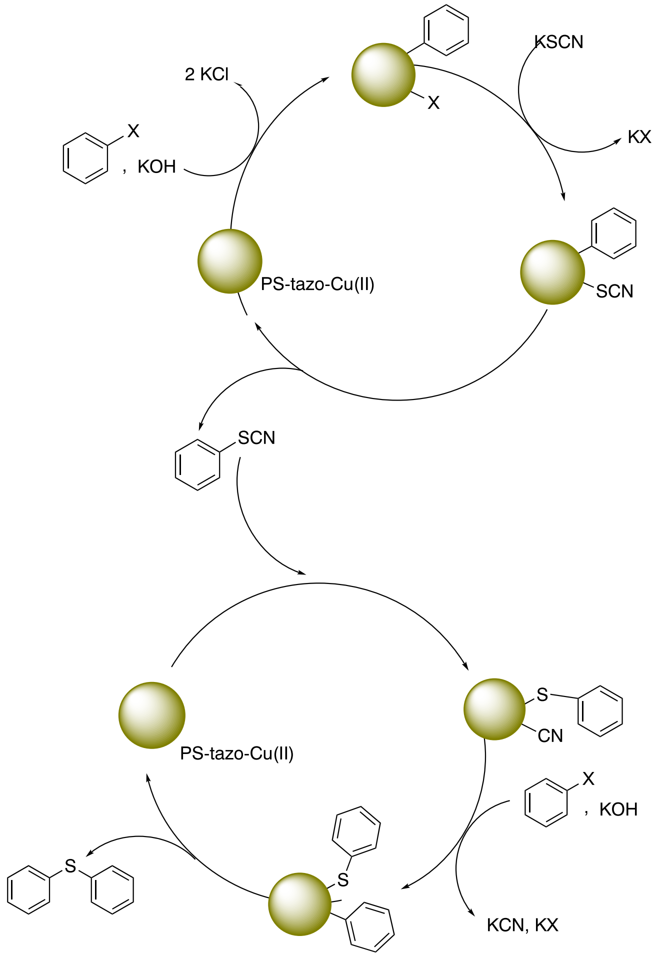
[a] Reaction conditions: iodobenzene (2 mmol), KSCN (1 mmol), base (4 mmol), H_2O (3 ml), additive (0.2 mmol), 135°C, aerobic conditions.
[b] Isolated yield.
[c] PEG-400: poly(ethylene glycol) 400.
[d] TBAB: tetrabutylammonium bromide.
[e] Reaction was done by CTAB (0.1 mmol).
[f] Reaction was done in 120°C.

Table 2. Scope of reaction of aryl halides and potassium thiocyanate, catalyzed by PS-tazo-Cu(II)[a]



Entry	X	Y	Time (h)	Product	Yield (%)[b]
1	I	H	7	**6a**	95
2	I	$4\text{-}NO_2$	7	**6b**	100
3	I	$3\text{-}NO_2$	7	**6c**	100
4	I	4-Cl	7	**6d**	100
5	I	4-Br	7	**6e**	100
6	I	$4\text{-}CH_3$	7	**6f**	90
7	I	$4\text{-}OCH_3$	7	**6 g**	88
8	Br	H	10	**6a**	83
9	Br	$4\text{-}NO_2$	10	**6b**	85
10	Br	$4\text{-}COCH_3$	10	**6 h**	80
11	Br	4-CHO	10	**6i**	78
12	Br	4-CN	10	**6j**	88
13	Br	$4\text{-}OCH_3$	10	**6f**	80
14	1-Br	Naphthalene	10	**6 k**	77
15	Cl	H	12	**6a**	62
16	Cl	$4\text{-}NO_2$	12	**6b**	69
17	Cl	4-Cl	12	**6d**	66
18	Cl	$4\text{-}NH_2$	12	**6 l**	55
19[c]	I	H	4	**6a**	95
20[d]	Br	H	7	**6a**	90

[a] Reaction conditions: aryl halide (2 mmol), KSCN (1 mmol), KOH (4 mmol), PS-tazo-Cu(II) (0.05 mmol of Cu), CTAB (0.2 mmol), H_2O (3 ml), 135°C, aerobic conditions.
[b] Isolated yield.
[c] Reaction of iodobenzene with thiophenol.
[d] Reaction of bromobenzene with thiophenol.



Scheme 2. Proposed mechanism for thioetherification of aryl halides with KSCN.

Table 3. Recyclability of catalyst under optimum reaction conditions[a]

Entry	Cycle	Yield (%)[b]
1	1	95
2	2	95
3	3	93
4	4	90
5	5	89

[a] Reaction conditions: iodobenzene (2 mmol), KSCN (1 mmol), KOH (4 mmol), PS-tazo-Cu(II) (0.05 mmol of Cu), CTAB (0.2 mmol), H_2O (3 ml), 135°C, aerobic conditions.
[b] Isolated yield.

(2.0 mmol), CTAB (0.2 mmol), PS-tazo-Cu(II) (0.05 mmol of Cu) and 3 ml of water. The mixture was heated under reflux at 135°C in an oil bath for 7 h under aerobic conditions. The progress of the reaction was monitored using TLC (n-hexane). After completion of the reaction, the copper catalyst was separated from the mixture by simple filtration, washed with water and ethyl acetate and reused in the next run. The organic layer was extracted using saturated brine solution. The solvent was removed under vacuum, and the product was purified using silica gel column chromatography with ethyl acetate–methanol as eluent.

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