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FULL PAPER

CuI heterogenized on thiosemicarbazide modified-multi walled carbon nanotubes (thiosemicarbazide-MWCNTs-CuI): Novel heterogeneous and reusable nanocatalyst in the C-N Ullmann coupling reactions

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Hojat Veisi, Department of Chemistry, Payame Noor University, Tehran, Iran. Email: hojatveisi@yahoo.com Herein we described the synthesis of novel thiosemicarbazide-MWCNTs-CuI nanocatalyst by covalent grafting of thiosemicarbazide on carbon nanotubes surface and subsequent coordination with CuI catalyst. The formation of nanocatalyst was analyzed by Raman spectroscopy, energy dispersive spectroscopy (EDS), wavelength-dispersive X-ray spectroscopy (WDX) and ICP analysis. The morphology of the nanocatalyst was characterized using scanning and transmission electron microscopes (SEM and TEM). Additionally, the (thiosemicarbazide-MWCNTs-CuI) nanocatalyst was successfully employed in the *N*-arylation of indole, amines and imidazoles through intermolecular C(aryl)-N bond formation from the corresponding aryl halides (Ar–I, Ar–Br, Ar–Cl) with amines through Ullmann-type coupling reactions. Interestingly, the novel catalyst could be recovered and recycled five times.

KEYWORDS

C-N bond formation, CuI, nanocatalyst, thiosemicarbazide, Ullmann

1 | INTRODUCTION

Carbon nanotubes including single-walled (SWCNT) and multi-walled (MWCNT) nanotubes have attracted considerable interests due to their remarkable thermal conductivity,^[1-3] mechanical,^[4-6] and electrical properties.^[6,7] In addition, their excellent chemical and mechanical stability and large surface area make them an ideal and potentially useful choice for applications in optics.^[7,8] electronics,^[9] catalysis,^[10,11] polymer composites,^[12] and many others.^[13] In this context, the deposition of the metal nanoparticles on carbon nanotubes (also referred to as "decoration") has provided further promising utilities for these materials in a wide range of applications from hydrogen storage, solar cells, sensor devices, energy storage, as well as catalysis.^[14,15] As such, one of the potential areas in which carbon nanotubes may be utilized as an effective solid support is in cross coupling reactions.[16-20]

The *N*-arylation of nitrogen-containing heterocycles is of particular interest as the resulting products represent important structural motifs of numerous natural products and biologically active compounds.^[21–24] Thus, the development of corresponding convenient and efficient synthesis methods have attracted considerable attention. In the successful C-N coupling methods, palladium,^[25] nickel^[26] and copper^[27] catalysts have been employed in the coupling of nucleophilic aromatic substitution with aryl halides. The lower cost of copper-based catalytic systems makes them particularly suitable for large-scale industrial applications and has challenged synthetic chemists to devise milder synthetic methods.

Traditionally, these compounds were prepared mostly by Ullmann-type coupling reactions. However, these reactions usually proceeded at high temperatures (around 200 °C) and often required using stoichiometric amounts of copper reagents, which make their further applications limited.^[28] To overcome these drawbacks, great progresses have been made on the modification of Ullmann-type coupling reactions.^[29-33] A recent notable achievement has been made by Buchwald and co-workers who discovered that in the presence of bidentate N,N-ligands, the Cu-catalyzed Narylation of nitrogen-containing heterocycles with aryl halides could be achieved in good yields under mild conditions.^[30] Following these pioneering works, a number of other groups have reported similar approaches for these reactions under mild conditions, with different kinds of copper compounds and appropriate bidentate N,N-, N,O- or O,Oligands.^[31] However, the coupling partners of nitrogen containing heterocycles were generally confined to aryl iodides and bromides. There are only a few reports where aryl chlorides were used as coupling partners.^[31-33] However, this advance in the field of Ullmann coupling is not sufficient as most of the reactions still require longer reaction time, high reaction temperature (more than 100 °C), and in some cases high catalytic loading. Therefore a mild, economic, and efficient catalytic system is still desirable for this process.

As a part of our ongoing research toward copper-catalyzed oxidation chemistry, very recently we reported CuI/metformin complex as a novel and efficient catalyst for C-N and C-O cross-coupling reactions via Ullmann-type coupling.^[34] So, encouraged by our previous works on C-C, C-N and C-O coupling reactions,^[35] we have designed an efficient approach for the preparation of thiosemicarbazide-functionalized multi walled carbon nanotubes anchored CuI (thiosemicarbazide-MWCNTs-CuI) (Scheme 1) and their application as heterogeneous catalyst in C(aryl)-N bond formation from the corresponding aryl halides (Ar–I, Ar–Br, Ar–Cl) with amines through Ullmann-type coupling reactions (Scheme 2).

2 | EXPERIMENTAL

2.1 | Materials

All the reagents were purchased from Aldrich and Merck and were used without any purification. The pure MWCNTs



SCHEME 1 Schematic diagram of thiosemicarbazide-MWCNTs-CuI fabrication



SCHEME 2 C(aryl)-N bond formation through Ullmann-type coupling reactions

without functional groups were purchased from Petrol Co. (Tehran, Iran). HCl, H_2SO_4 , HNO₃, deionized water, NaH (80%), triethylamine, acetonitrile, CuI, thiosemicarbazide and *N*,*N*-dicyclohexylcarbodiimide (DCC) were obtained from Sigma Aldrich and Merck.

2.2 | Preparation of thiosemicarbazide-MWCNTs

The thiosemicarbazide-MWCNTs were prepared according to the literature.^[36]

2.3 | Heterogenization of CuI on the surface of thiosemicarbazide-MWCNTs

1.0 mmol of CuI was dissolved in 50 mL of DMF 50 °C for 0.5 h. Then 1.0 g of thiosemicarbazide-MWCNTs solid that before sonicated in 50 mL DMF, was added and stirred at room temperature for 24 h. After completion of the reaction, solid product was filtered, washed with DMF, acetone and ethanol and dried in vacuum at 80 °C for 24 h to give thiosemicarbazide-MWCNTs-CuI. Elemental analysis of the thiosemicarbazide-MWCNTs-CuI using ICP-AES gave a 0.32 mmol/g loading of copper.

2.4 | *N*-Arylation of indoles in the presence of thiosemicarbazide-MWCNTs-CuI

In a 25 mL balloon, the catalyst (30 mg catalyst =0.01 mmol CuI), aryl halides (1 mmol), DMF (3 mL), indole (1 mmol), and Et₃N (2 mmol) were added. The mixture was then stirred for the desired time at 80 °C. The reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by centrifuge and washed with ethyl acetate and ethanol. The combined organic layer was dried over anhydrous sodium sulfate and evaporated in a rotary evaporator under reduced pressure. The resultant material was purified by preparatory TLC with silica gel to afford the desired product.

3 | RESULTS AND DISCUSSION

The thiosemicarbazide-functionalized Multi-Walled Carbon Nanotubes (thiosemicarbazide-MWCNTs) was conveniently synthesized according to the report by Jie Zhang.^[36] Next, CuI coordinated on the surface of the thiosemicarbazide-MWCNTs. The loading of Cu in the obtained material was determined by inductively coupled plasma (ICP) analysis to be 0.32 mmol/g. The pathways of thiosemicarbazide-MWCNTs-CuI fabrication are shown in Scheme 1.

The morphology of the thiosemicarbazide-MWCNTs-CuI was characterized by field emission scanning electron microscopy (FE-SEM) in Figure 1. It is observed that in the image, the surface of CNTs uniformly coated, thus clearly indicative the successful functionalization of MWCNTs.

The EDS analysis was employed to determine the chemical composition of the synthesized thiosemicarbazide-MWCNTs-CuI (Figure 2). The EDS spectra showed well defined peaks of C, N, O, S, Cu and I, thereby confirming the successful anchoring of the CuI on the thiosemicarbazide-MWCNTs surface.

The wavelength-dispersive X-ray spectroscopy (WDX)coupled quantified FESEM mapping of the sample was also investigated (Figure 3). The wavelength-dispersive X-ray spectroscopy (WDX) can provide qualitative information about the distribution of different chemical elements in the catalyst matrix. Looking at the compositional maps of C, N, S, Cu, I, and mainly the combined composition image, the presence of Cu ions with good dispersion is clearly distinguished in the composite. Also, the presence of nitrogen in the composite indicated the successful functionalization of CNTs with thiosemicarbazide.



FIGURE 1 SEM images of thiosemicarbazide-MWCNTs-CuI



FIGURE 2 Energy-dispersive X-ray spectroscopy (EDX) of the thiosemicarbazide-MWCNTs-CuI

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and possible grafting of thiosemicarbazide groups supported on MWCNTs. The existence of thiosemicarbazide groups that bonded on MWCNTs was clearly distinguishable as identified spots in Figure 4. This result indicates that the CNTs were covalently grafted by thiosemicarbazide.

Another method for assessment of functionalization reaction is Raman spectroscopy. Figure 5 shows the Raman spectra of the samples. Two main peaks in the Raman spectra were appeared in the samples at 1338 and 1596 cm⁻¹ which are known as D and G bonds, respectively. D band is related to disordered carbon atoms of MWCNTs corresponding to sp³ hybridized and G band shows the sp²-hybridized of carbon atoms in the graphene sheets. Area ratio of the D to G bands (I_D/I_G) can be used to assess the amount of defects in nano particles structure. ID/IG ratio was increased for thiosemicarbazide-MWCNTs ($I_D/I_G = 1.24$) which approves the successful conversion of MWCNTs to thiosemicarbazide -MWCNTs. In the absence of amorphous carbon, the increase of ID is related to increase of carbon containing sp³ hybridized and implies to successful functionalization reaction.

In our initial screening experiments, the *N*-arylation reaction of indole with iodobenzene was investigated to optimize the reaction conditions including CuI concentration, solvent, bases and temperature without the protection by an inert gas, and the results are summarized in Table 1.

Initially, various solvents such as DMF, EtOH, CH_3CN , Toluene, CH_2Cl_2 , DMSO and H_2O were studied in the presence of 20 mg catalyst =0.01 mmol CuI, and 2 equiv, of Et_3N at 80 °C (Table 1, entries 1–7). As could be seen in the Table 1, the best result was obtained in DMF (Table 1, Entry 7). Next, the bases, including Et_3N , KOH, K_3PO_4 , Na_2CO_3 , NaHCO₃ and K_2CO_3 were explored, and Et_3N gave the best yields (Table 1, entries 1, 12–16). However, a low yield was obtained without any base (Table 1, entry 10). It was also



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FIGURE 3 FESEM image of thiosemicarbazide-MWCNTs-CuI, and elemental maps of C, N, S, I and Cu atoms



FIGURE 4 TEM images of thiosemicarbazide-MWCNTs-CuI



FIGURE 5 Raman spectra of the (a) MWCNTs, and (b) thiosemicarbazide-**MWCNTs**

found that the reaction temperature has a great influence on this transformation (Table 1, entries 9, 17, 18). The obvious improvement in the conversion (96%) was achieved for the reaction at 80 °C (Table 1, entry 9).

In addition, when the amount of catalyst was increased from 20 mg to 30 mg (30 mg catalyst =0.01 mmol CuI), the excellent yield was also afforded. However, when 10 mg of catalyst was employed, the reaction yield decreased to 60% (Table 1, entries 7–9). It is important to mention that N-arylation of indole did not take place in absence of CuI catalyst (Table 1, entry 11). In summary, the optimal condition for the N-arylation of indole with iodobenzene involves the use of 30 mg catalyst =0.01 mmol CuI, 2 equiv. of Et₃N in DMF at 80 °C for 2 h (Table 1, Entry 9).

Having established the optimized reaction conditions, we then carried out the reaction of indole with aromatic compounds with different leaving groups, such as I-, Br-, and Cl-. As shown in Table 2, the reaction of iodides and

TABLE 1	Optimization	of reaction	condition	for the	N-arylation	of indole
with iodobe	enzene ^a					

	H + H + H H H N N N N N N N N N N N N N					
Entry	Catalyst (mg)	Base	Solvent	T (°C)	t (h)	Yield (%) ^b
1	20	Et ₃ N	CH ₃ CN	82	12	45
2	20	Et ₃ N	EtOH	78	12	50
3	20	Et ₃ N	Toluene	110	12	70
4	20	Et ₃ N	H_2O	100	12	25
5	20	Et ₃ N	CH_2Cl_2	40	12	35
6	20	Et ₃ N	DMSO	80	12	90
7	20	Et ₃ N	DMF	80	3	92
8	10	Et ₃ N	DMF	80	12	60
9	30	Et ₃ N	DMF	80	2	96
10	30	-	DMF	80	24	Trace
11	0.0	Et ₃ N	DMF	80	24	0
12	30	K_2CO_3	DMF	80	2	70
13	30	Na ₂ CO ₃	DMF	80	2	50
14	30	K_3PO_4	DMF	80	2	60
15	30	KOH	DMF	80	2	75
16	30	NaHCO ₃	DMF	80	2	55
17	30	Et ₃ N	DMF	25	2	Trace
18	30	Et ₃ N	DMF	60	2	55

^aReaction conditions: indole (1.0 mmol), iodobenzene (1.1 mmol), catalyst, base (2.0 mmol), solvent (5.0 mL).

^bIsolated yield.

 TABLE 2
 Synthesis of N-aryl-amines catalyzed by thiosemicarbazide-MWCNTs-Cul^a

Ar-X + Het-NH thiosemicarbazide-mwCn1s-Cui → Ar-N-Het Et ₃ N, DMF, 80°C						
Entry	Aryl halides	amines	Time (h)	Yield $(\%)^{b}$	Ref.	
1	Ph-I	Indole	2	96	[31]	
2	Ph-Br	Indole	3	92	[31]	
3	Ph-Cl	Indole	10	75	[31]	
4	4-Me-Ph-I	Indole	1.5	96	[31]	
5	4-Me-Ph-Br	Indole	4	90	[31]	
6	4-Me-Ph-Cl	Indole	12	80	[31]	
7	4-MeO-Ph-I	Indole	2	96	[31]	
8	4-MeO-Ph-Br	Indole	3	90	[31]	
9	4-MeO-Ph-Cl	Indole	12	95	[31]	
10	Ph-I	1H-imidazole	3	96	[37]	
11	Ph-Br	1H-imidazole	6	80	[37]	
12	Ph-Cl	1H-imidazole	24	65	[37]	
13	Ph-I	1H-pyrazole	3	95	[37]	
14	Ph-Br	1H-pyrazole	5	90	[37]	
15	Ph-Cl	1H-pyrazole	24	70	[37]	
16	Ph-I	Aniline	1	98	[37]	
17	Ph-Br	Aniline	3	90	[37]	
18	Ph-Cl	Aniline	5	75	[37]	

^aReactions were carried out under aerobic conditions in 5 mL of DMF, 1.1 mmol aryliodides, 1.0 mmol amines and 2 mmol Et_3N in the presence of CuI nanocatalyst (30 mg, 0.02 mmol Cu) and 80 °C.



FIGURE 6 The recycling of the thiosemicarbazide-MWCNTs-CuI

bromides were proceeded rapidly and efficiently to obtain the product (Table 2, entries 1, 2, 4, 5, 7, 8). However, lower yield were obtained when the leaving group was changed to chlorides (Table 2, entries 3, 6, 9). These results ascertained the order of reactivity: R-I > R-Br > R-CI. This protocol not only significantly improved the yields, but also the process took place in shorter reaction times under mild conditions in comparison to the previously known procedures.

To further explore the scope of this protocol, we decided to investigate this Ullmann-type C-N coupling reaction of other amines (imidazole, pyrazole and aniline) with aryl halides (Table 2. entries 10–18). The desired products were obtained in moderate to good yield. It is very important to mention that the reaction is very selective to give only *N*-arylated product and in none of these cases C-arylation of amine was observed.

In order to determine whether the catalysis was due to the thiosemicarbazide-MWCNTs-CuI complex or to a homogeneous CuI complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.^[38] We focused on the N-arylation reaction of indole with iodobenzene. We filtered off the thiosemicarbazide-MWCNTs-CuI complex after 30 minutes of reaction time and the filtered phase of the reaction mixture was kept in reaction condition for another 2 h. The catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid possible recoordination or precipitation of soluble CuI upon cooling. The reaction of indole with iodobenzene at 80 °C for 30 minutes before the hot filtration could afford N-phenylindole in 45% yield. We found that, after this hot filtration, no further reaction was observed. This result suggests that the CuI catalyst remains on the thiosemicarbazide-MWCNTs support at elevated temperatures during the reaction and points to a process of heterogeneous nature.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability, and reusability. The recycling performance of thiosemicarbazide-MWCNTs-CuI was investigated in the reaction of iodobenzene and indole. Thiosemicarbazide-MWCNTs-CuI was centrifuged from the reaction, washed

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with hot ethanol and water, and reused in a next reaction. The data listed in Figure 6 show that catalyst could be reused 5th times with only marginal loss of its catalytic activity. The high stability and excellent reusability of the catalyst should result from the chelating action of thiosemicarbazide groups on CuI and the mesoporous structure of the MWCNTs support.

4 | CONCLUSION

In this study, thiosemicarbazide was successfully bonded on the surface of MWCNTs to subsequent coordination by CuI as a novel nanocatalyst. Raman spectroscopy, EDS, WDX, TEM, FESEM and ICP analysis confirmed the structure of the nano composite. The (thiosemicarbazide-MWCNTs-CuI) nanocatalyst was successfully employed in the *N*-arylation of indole, amines and imidazole through intermolecular C(aryl)-N bond formation from the corresponding aryl halides (Ar–I, Ar–Br, Ar–Cl) with amines through Ullmann-type coupling reactions. The catalyst showed good stability and could be reused 5 times with only marginal loss of its catalytic activity.

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