FULL PAPER



Copper containing nanosilica thioalated dendritic material: A recyclable catalyst for synthesis of benzimidazoles and benzothiazoles

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Majid Moghadam, Valiollah Mirkhani and Shahram Tangestaninejad, Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan, 81746-73441 Iran. Email: moghadamm@sci.ui.ac.ir; mirkhani@sci.ui.ac.ir; stanges@sci.ui.ac.ir In this paper, the design and characterization of a new heterogeneous catalyst by incorporation of copper ions into the nanosilica modified by thiole–based dendrimer are reported. The prepared catalyst was characterized by FT–IR, TGA, elemental analysis, FE–SEM, TEM, XPS and ICP–OES techniques. This material was used as catalyst in the synthesis benzimidazoles and benzothiazoles by the reaction of substituted benzaldehydes with 1,2–diaminobenzene or 2–aminothiophenol, respectively. The advantages of the present catalytic system are high yields, mild conditions and short reaction times. On the other hand, this new synthesized catalyst was recycled very well and reused several times without significant loss of its catalytic activity.

KEYWORDS

benzimidazole, benzothiazole, dendritic polymer, nanosilica

1 | **INTRODUCTION**

Benzimidazoles and benzothiazoles are of considerable importance in biological applications.^[1–3] These compounds are crucial core structures used to produce drugs and materials. They show medicinal activities such as anticancer,^[4] antiulcer,^[5] antihypertensive,^[6] antibacterial,^[7] and enzyme inhibition.^[8,9] They have also been applied in dyes,^[10] chemosensing,^[11] fluorescence, and corrosion science.^[12–14] Considering the importance of these heterocycles in vital applications, proposing of milder, novel, sustainable and cheaper processes for the design and assembly of the benzimidazoles and benzothiazoles is imperative.

These compounds have been synthesized previously in different conditions, like using various types of catalysts,^[15–17] solvent free^[18] or catalyst free^[19] reactions.

The direct functionalizing of covalent bond using transition metal catalysts has been attracted lots of attentions due to its developing applicability.^[20–22] Ruthenium^[23,24] rhodium^[25–28] and palladium^[29–33] as precious metals used to be the most important part of these catalytic reactions. The mentioned metals have been employed to catalyze both C–C and C–X (X = heteroatom) synthesis from the starting C–H bond.^[34–36] Recently, much more attention has been attracted into reducing the use of these precious metals in catalytic reactions due to their cost and limited availability. Copper is a great substitution in this case because of its low toxicity and low price^[37,38] This metal is the key catalyst in different useful methods for the synthesis of biological molecules and chemical compounds. For example, it is applied for N–arylation.^[39–42] S–arylation^[43,44] O–arylation^[45,46] and C–arylation.^[47,48] It is also reported as an efficient catalyst for the Suzuki–Miyaura^[49,50] and Sonogashira cross–coupling reactions^[51]

Recent advances in the chemistry of dendrimers, make them largely suitable for catalysis. Dendrimers are very well-defined, mono-sphere, three-dimensional polymers. However, dendrimers architecture makes them able to host metals in their uncountable cavities and also by coordination to their functional groups. These composites are also excellent scaffolds for catalyst structures.^[52,53] Recently, we reported the application of triazine dendritic materials containing Pd, Cu, Bi, Au and Ru in organic synthesis.^[54–61]

In continuation of our previous works on the use of dendritic materials, here, we wish to report the preparation and characterization of a thiol–based dendritic material containing Cu(II) species. These copper species are the key point for the catalytic synthesis of benzmidazoles and benzothiazoles from corresponding aldehydes (Scheme 1).

2 | EXPERIMENTAL

2.1 | General remarks

All reagents were purchased from Merck, Fluka and Sigma-Aldrich. All reagents and solvents were used without further purification. The activated nano - silica was prepared as described in the literature.^[62,63] FT - IR spectra were recorded on a Jasco 6300D instrument in the range of $400-4000 \text{ cm}^{-1}$. The UV-vis diffuse reflectance spectra of the samples were obtained by a JASCO V-670 spectrophotometer. Thermal gravimetric analysis (TGA) was recorded on a Mettler TG50, under air flow at a consistent heating of 5 °C min⁻¹ in the range of 0–600 °C. Elemental analysis was obtained on a LECO CHNS - 932 analyzer. X-ray photoelectron spectra (XPS) were recorded on an XPS-Auger Perkin Elmer 8025-BesTec electron spectrometer. This instrument includes an ultra-high vacuum chamber, a hemi-spherical electron energy analyzer and an X-ray source providing unfiltered K_{α} radiation from its Al anode $(h\nu = 1486.6 \text{ eV})$. The pressure of the main spectrometer chamber during data acquisition was maintained at ca. 10^{-7} Pa. The binding energy (BE) scale was calibrated by using the peak of adventitious C 1 s, setting it to 284.5 eV. The accuracy of the BE scale was ± 0.1 eV. The copper content of the catalyst was measured by an inductively coupled plasma optical emission spectrometry (ICP – OES), via a Jarrell – Ash 1100 ICP analyzer. Scanning electron microscopy images were performed on a Hitachi S - 4700 field



SCHEME 1 Synthesis of benzimidazoles and benzothiazoles catalyzed by cu(II)-TD@nSiO₂

emission – scanning electron microscope (FE – SEM). Transmission electron microscopy (TEM) measurements were carried out on a Philips CM10 analyser operating at 100 kV. The nano – silica supported thiolated dendritic polymer (G2 or nSTDP) was prepared according to our recently reported procedure.^[64]

2.2 | Synthesis of nanosilica triazine dendrimer containing cu(II) species (cu(II)– TD@nSiO₂)

In a round bottomed flask, $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ (0.4 mmol) was added to a stirring mixture of nano-silica supported dendrimer (G2) (0.5 g) in DMF (10 ml). The slurry mixture was stirred at room temperature for 12 h, and filtered by a Buchner funnel with a sintered glass disc. The solid material was washed continuously with acetone (3 × 10 ml) and then dried in a vacuum oven at 50 °C. Finally, Cu(II)–TD@nSiO₂ catalyst was obtained as a greenish blue solid.

2.3 | Typical procedure for synthesis of benzimidazoles or benzothiazoles catalyzed by cu(II)-TD@nSiO₂

In a round–bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of aldehyde (1 mmol), 1,2– phenylenediamine or 2–aminithiophenol (1 mmol) and Cu(II)–TD@nSiO₂ (5 mg, containing 0.0012 mmol Cu(II)) in EtOAc (2 mL) was prepared and stirred at 50 °C. The progress of the reaction was tracked by TLC (eluent: *n*–hexane/EtOAc, 4:1). At the end of the reaction, the reaction mixture was cooled to room temperature and EtOAc/EtOH (3:2, 15 ml) was added. The catalyst was filtered and washed with EtOAc (3 × 5 ml). The filtrate was evaporated and the product was purified by recrystallization from EtOAc or EtOH (depends on the polarity of the product).

3 | **RESULTS AND DISCUSSION**

3.1 | Preparation and characterization of the catalyst, Copper(II) encapsulated in nanosilica thiolated dendric polymer

The TD@nSiO₂ dendrimer was prepared and characterized according to our recently published literature.^[64] The G2– dendrimer with SH groups on its outer periphery is suitable for encapsulation of Cu(II). As shown in Scheme 2, the copper (II) particles immobilized on nano – silica thiolated dendritic polymer (Cu(II)–TD@nSiO₂) were obtained by the reaction of CuBr₂·2H₂O with nSTDP in DMF at room temperature. Providing evidence of copper presence, copper content of the catalyst was measured by ICP, which showed



 $\label{eq:schemes} \textbf{SCHEME 2} \quad Preparation \ of \ the \ Cu(II) - TD@nSiO_2 \ catalyst$

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a value of 0.254 mmol per gram of Cu(II)–TD@nSiO $_{2}$ catalyst.

The FT – IR spectrum of G2 and Cu(II)–TD@nSiO₂ (Figure S1a and b) were in a good accordance which shows almost no specific change in dendrimer structure after hosting Cu(II) particles. This is due to the low copper loading of the catalyst which shows no obvious change compared to the support.

The diffuse reflectance UV–vis spectra of G2 and Cu(II)– TD@nSiO₂ are compared in Figure S2. The new broad bands of low intensity centred at 700 and ~850 nm (Figure S2b) which are usually assigned to a *d*–*d* transitions, indicating that the solid is a copper(II) compound, Cu(II)– TD@nSiO₂.^[65] Also an intense peak at ~310 nm is assigned to the moderate ligand–to–metal charge transfer transition from p_{π} orbitals of the donor atoms to d orbitals of Cu(II).^[66]





(b)

 $\label{eq:FIGURE 1} FE-SEM \ images \ of: a) \ nSTDP \ and \ b) \ cu(II)-TD@nSiO_2$





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FIGURE 2 (a) TEM image of cu(II)–TD@nSiO₂ and (b) particle size distribution histogram of cu(II)–TD@nSiO₂

Figure 1a and b present the FE – SEM images of nSTDP and Cu(II)–TD@nSiO₂. The size and surface morphologies of the nSTDP and Cu(II)–TD@nSiO₂ are uniform, as it shows in the images, the nSiO₂ particles are spherical and the average diameters are in the range of 50 to 70 nm. The energy dispersive X – ray (EDX) results, collected from SEM analysis, proved the presence of sulfur in the nSTDP and also copper element in the Cu(II)–TD@nSiO₂ (Figures S3 and S4).

Figure 2a, shows the transmission electron microscopy (TEM) image of the copper containing dendrimer. The dark colored area of the photo is because of higher electron density of copper in comparison with nanosilica.^[67] Also, the dendrimers agglomerate and local higher densities of copper salts are observed. The histogram of size distribution showed that the matrix has an average diameter of about 15–30 nm (Figure 2b).

X-ray photoelectron spectroscopy (XPS) is a powerful tool for assessing the chemical composition of macromolecules, ligands and mixed valent complexes via investigation of electron properties of the species formed on the surface, such as the electron environment, oxidation state, and the binding energy of the core electron of the metal.^[68]

The XPS spectrum of catalyst from 0.0 to 1200.0 eV is shown in Figure 3a. In this spectrum, the characteristic binding energies of C 1 s, Si 2p, O 1 s, S 2 s, S 2p and Cu 2p are identified. In general, the binding energy at 102.40 eV is due



FIGURE 3 The XPS spectra of catalyst: (a) the elemental survey spectrum, (b) showing cu $2p_{3/2}$ and cu $2p_{1/2}$ binding energies

to Si 2p in the nSiO₂ and the binding energy at 532.1 eV is attributed to O 1 s in Si-O network.^[69] Furthermore, the presence of Cu(II) ions was also confirmed by X-ray photoelectron spectroscopy. The XPS analysis of Cu(II) in the catalyst shows two intense peaks at 932-935 eV and 952–955 eV, corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks. Each of the Cu 2p peaks in the spectrum of the catalyst was fitted using two Gaussian-Lorentzian peaks with energies of 934.32 and 932.99 eV for Cu 2p3/2, and 953.89 and 952.72 eV for Cu $2p_{1/2}$ (Figure 3b). The peak at 934.32 eV (90.36%) corresponds to Cu(II) ions while the lower peak at 932.99 eV (9.64%) corresponds either to Cu(I) or Cu(0), though the chemical states of Cu(I) and Cu(0) are not distinguishable by XPS analysis.^[70] The presence of reduced forms of Cu(II) has been described by Hwang and Woo^[71] who have reported that Cu(II) is reduced to the lower oxidation states under X-ray irradiation in Ultrahigh vacuum (by calcination followed by heating in He). The peaks corresponding to sulfur are also clearly observed in XPS elemental survey of the catalyst at 224.8 eV (S 2 s) and 164.7 eV (S $2p_{3/2}$), respectively (Figure 3a).^[69]

All above observations confirm that the thiolated dendritic polymer is an appropriate host and ligand for copper(II) particles.

3.2 | Catalytic experiments

The catalytic activity of the prepared catalyst was investigated in the synthesis of benzimidazoles and benzothiazoles.

$\bigcup_{ZH} \xrightarrow{H}_{CI} \xrightarrow{CHO} \xrightarrow{CHO} \xrightarrow{CHO} \xrightarrow{N}_{Z} \xrightarrow{CI}$								
Z= NH, S Entry ZH Catalyst (mg) Solvent T (°C) Time (min) Yield (%) ^a								
1	NH ₂	-	EtOAc	50	15	—		
2	NH ₂	$n-SiO_2(5)$	EtOAc	50	15	8		
3	NH_2	$TD@nSiO_2(5)$	EtOAc	50	15	10		
4	NH ₂	Cu(II)@nSiO ₂ (5)	EtOAc	50	15	84		
5	NH_2	Cu(II)-TD@nSiO ₂ (10)	EtOAc	50	15	100		
6	NH ₂	Cu(II)–TD@nSiO ₂ (5)	EtOAc	50	15	100		
7	NH ₂	Cu(II)-TD@nSiO ₂ (5)	_	50	15	_		
8	NH ₂	Cu(II)–TD@nSiO ₂ (5)	<i>n</i> -hexane	50	15	45		
9	NH ₂	Cu(II)–TD@nSiO ₂ (5)	THF	50	15	65		
10	NH ₂	Cu(II)-TD@nSiO ₂ (5)	CH ₃ CN	50	15	93		
11	NH ₂	Cu(II)–TD@nSiO ₂ (5)	H_2O	50	15	25		
12	NH ₂	Cu(II)–TD@nSiO ₂ (5)	DMF	50	15	86		
13	NH ₂	Cu(II)-TD@nSiO ₂ (5)	EtOAc	25	15	75		

 TABLE 1
 Optimization of the conditions for synthesis of benzimidazoles and benzothiazoles

TABLE 1 (Continued)

		211 01				
		Z= NH, S				
Entry	ZH	Catalyst (mg)	Solvent	T (°C)	Time (min)	Yield (%) ^a
14	NH ₂	Cu(II)–TD@nSiO ₂ (5)	EtOAc	75	15	100
15	NH ₂	Cu(II)-TD@nSiO ₂ (5)	EtOAc	50	10	84
16	NH ₂	Cu(II)-TD@nSiO ₂ (5)	EtOAc	50	20	100
17	SH	Cu(II)-TD@nSiO ₂ (10)	-	25	15	96
18	SH	Cu(II)-TD@nSiO ₂ (5)	-	25	15	96
19	SH	Cu(II)-TD@nSiO ₂ (5)	-	50	15	96
20	SH	Cu(II)-TD@nSiO ₂ (5)	-	25	10	86
21	SH	Cu(II)-TD@nSiO ₂ (5)	-	25	20	96

^aIsolated yield.

$\frac{1}{R} + \frac{1}{NH_2} + \frac{1}{H_2} + \frac{1}{H_2} + \frac{1}{S0 \circ C, air} + \frac{1}{R} + \frac{1}{N} + \frac{1}{N}$						
Entry	R	Ar	Product	Time (min)	Yield (%) ^b	TOF (h^{-1})
1	Н	Ph		20	95	2398
2	Н	4-cl-C ₆ H ₄	N	15	100	3333
3	Н	$4-Br-C_6H_4$	N N H Br	18	94	2611
4	Н	4-me-C ₆ H ₄	N N CH_3	35	96	1379
5	Н	9–Anthracenyl		35	90	1293
6	4cl	1–Naphthyl		55	90	819
7	4-me	1–Naphthyl		50	94	943
8	Н	3–Pyridyl		80	90	563
9	4-me	3–Indolyl	NH NH	80	88	551

 TABLE 2
 Synthesis of benzimidazoles catalyzed by cu(II)-TD@nSiO2^a

^aReaction conditions: aldehyde (1 mmol), 1,2-phenylenediamine (1 mmol), Cu(II)-TD@nSiO₂ (5 mg, 0.0012 mmol Cu(II)), EtOAc (2 ml), 50 °C. ^bIsolated yield.

TABLE 3 Synthesis of benzothiazoles catalyzed by cu(II)-TD@nSiO2^a

$ \begin{array}{c} & & \\ & & $						
Entry	Ar	Product	Time (min)	Yield (%) ^b	TOF (h^{-1})	
1	Ph		20	90	2272	
2	4–ClC ₆ H ₄		15	96	3200	
3	$4-BrC_6H_4$		20	89	2247	
4	4–MeC ₆ H ₄	CH ₃	18	98	2722	
5	3-MeOC ₆ H ₄	OMe	35	95	1364	
6	1–Naphthyl		50	92	923	
7	3-NO ₂ C ₆ H ₄	$ \underset{S}{\overset{NO_2}{\longrightarrow}} $	100	85	426	
8	3–Indolyl	NH S	80	95	595	

^aReaction conditions: aldehyde (1 mmol), 2-aminothiophenol (1 mmol), Cu(II)-TD@nSiO₂ (5 mg, 0.0012 mmol Cu(II)), 25 °C. ^bIsolated yield.

3.2.1 | Synthesis of benzimidazoles and benzothiazoles catalyzed by cu(II)-TD@nSiO₂

Synthesis of benzimidazoles and benzothiazoles, typically require careful optimization of reaction parameters such as amount of Cu(II)–TD@nSiO₂ catalyst, solvent, temperature, and reaction time (Table 1).

For identifying the exact optimized conditions for the synthesis of benzimidazoles, the of 4reaction chlorobenzaldehyde with 1,2-phenylenediamine was selected as a model in the presence of Cu(II)-TD@nSiO₂ as catalyst. The model reaction was first carried out in the absence of the catalyst. No product was observed under these conditions (Table 1, entry 1). The reaction was then performed in the presence of nano-SiO2, TD@nSiO2, Cu(II) @nSiO₂^[59] and Cu(II)-TD@nSiO₂ (Table 1, entries 2-5). The results confirmed that Cu(II)-TD@nSiO₂ was an efficient catalyst in this reaction. The optimized conditions were obtained applying 5 mg of catalyst (containing 0.0012 mmol Cu(II)) in EtOAc at 50 °C within 15 min (Table 1, entry 6).

To find the optimized conditions for the synthesis of benzothiazoles, 2–aminothiophenol (1 mmol) was treated with 4–chlorobenzaldehyde (1 mmol) under conventional conditions. After some preliminary experiments (Table 1, entries 17–21), it was found that the best yield of the desired

benzothiazole can be obtained in the presence of 5 mg catalyst at room temperature within 15 min under solvent–free conditions.

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In order to explore the scope and generality of the prepared catalyst, the optimized reaction conditions were then applied for the synthesis of a series of benzimidazoles and benzothiazoles. As shown in Table 2, aromatic aldehydes bearing electron–donating and electron–withdrawing groups reacted efficiently with 1,2–phenylenediamines in the presence of catalytic amount of Cu(II)–TD@nSiO₂ at 50 °C to

TABLE 4Comparison of the results obtained in the synthesis of the
benzimidazole. Reaction of benzaldehyde with 1,2–phenylenediamine
catalyzed by cu(II)– $TD@nSiO_2$ with those obtained by the recently
reported catalysts

		TOF	
Catalyst	Reaction conditions	(h ⁻¹)	Ref
Cu(OH) ₂	Methanol/O ₂ /r.t	2.45	[72]
Copper dendrimer	EtOAc/ 50 °C	670.6	[38]
Copper triflate	CH ₃ CN/reflux/N ₂ atm	0.55	[73]
GLR-G2-cu polymer	Ethanol/ air/ 30 °C	1342	[74]
$Cu(II) - TD@nSiO_2$	EtOAc/ 50 °C	2398	This work

	Yield	(%) ^c	Cu(II) lea	Cu(II) leached (%) ^d		
Run	Benzimidazole	Benzothiazole	Benzimidazole	Benzothiazole		
1	100	96	0.8	1		
2	97	90	0.5	0.6		
3	95	90	0.4	0		
4	93	90	0	0		
5	93	90	0	0		

^aReaction conditions: aldehyde (1 mmol), 1,2-phenylenediamine (1 mmol), Cu(II)-TD@nSiO₂ (5 mg, 0.0012 mmol Cu(II)), EtOAc (2 mL), 50 °C.

^bReaction conditions: aldehyde (1 mmol), 2-aminothiophenol (1 mmol), Cu(II)-TD@nSiO₂ (5 mg, 0.0012 mmol Cu(II)), 25 °C.

^cIsolated yield.

^dMeasured by ICP analysis.

afford the corresponding benzimidazoles in high yields (94–100%) (Table 2, entries 1–4). Under the same reaction conditions, polycyclic aldehydes such as 9– anthracenecarboxaldehyde and 1–naphthaldehyde afforded the corresponding benzimidazoles in 90–94% yields (Table 2, entries 5–7). It is worth mentioning that heterocyclic aldehydes such as 3–pyridinecarboxaldehyde and indole–3– carboxaldehyde took part smoothly in the reaction to give the desired products in 88–90% yields (Table 2, entries 8, 9).

To further widen the applicability of the present methodology, the synthesis of benzothiazoles was investigated in the presence of Cu(II)–TD@ nSiO₂. As shown in Table 3, treatment of a variety of aldehydes with 2–aminothiophenol in the presence of catalytic amount of Cu(II)–TD@nSiO₂ at room temperature afforded the corresponding benzothiazoles in 85–96% yields.

The results of the present study were compared with some results reported in the benzimidazole synthesis catalysed by different copper containing catalysts. From the provided data in Table 4, this catalytic system is superior compared to the others.

3.3 | Reusability of the catalyst

From industrial and economic points of view, the catalyst recycling is the most important issue for a heterogeneous catalyst. Therefore, the reusability of the Cu(II)–TD@nSiO₂ catalyst was investigated in the benzimidazole synthesis of 4–chlorobenzaldehyde with 1,2–phenylenediamine and benzothiazole synthesis of 2–aminothiophenol with 4– chlorobenzaldehyde. After completion of each catalytic cycle, the catalyst was separated by filtration and reused. The results showed that the catalyst could be reused five consecutive times without significant loss of its catalytic activity in both reactions (Table 5). The analysis of copper leaching from Cu(II)–TD@nSiO₂ catalyst by ICP indicated that only

a negligible amount of copper (less than 1%) has been leached in the first three runs in the benzimidazole synthesis and in the first two runs in the benzothiazole synthesis.

4 | **CONCLUSIONS**

We have developed an efficient and scalable multi-step process for the synthesis of a new thiolated dendrimer which was precisely characterized. The obtained dendrimer was encapsulated by copper (II) and successfully utilized for the catalytic synthesis of benzimidazoles and benzothiazoles from corresponding aldehyde, diamine and aminothiophenol. The reusability of the catalyst was also investigated. Compared to deposited copper on nanosilica surface, our catalyst shows a better stability and recyclability.

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