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# Expeditious one-pot three component synthesis of *N*-aryl dithiocarbamate derivatives using mesoporous Cu-materials

Soumen Payra<sup>a</sup> Arijit Saha<sup>a</sup> Rui Peng<sup>b</sup> Chia-Ming Wu<sup>b</sup>, Ranjit T. Koodali<sup>b,\*</sup> and Subhash Banerjee<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Guru Ghasidas Vishwavidyalaya (a Central University), Bilaspur-495009, Chhattisgarh, India. <sup>b</sup>Department of Chemistry, The University of South Dakota, 414 E. Clark Street, Vermillion, SD, 57069, USA.

\*Corresponding authors, Email: <u>ocsb2009@yahoo.com</u> (S.B.); <u>ranjit.koodali@usd.edu</u> (R.T.K.)

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ABSTRACT

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Keywords: Mesoporous Cu-materials N-aryl dithiocarbamate derivatives Multicomponent reactions C-N and C-S bond formation In this study, a facile one-pot three component protocol has been demonstrated for the preparation of synthetically challenging *N*-aryl dithiocarbamate derivatives using mesoporous Cu-materials as catalyst at room temperature. The mesoporous Cu-catalysts namely Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15 were prepared by impregnation of Cu-salts on the synthesized mesoporous materials and were characterized by powder X-ray diffraction, N<sub>2</sub> adsorption-desorption, and transmission electron microscopic studies. Significant improvement of yields was obtained using mesoporous Cu-catalysts under milder reaction conditions compared to the earlier reported catalysts. All the three mesoporous Cu-catalysts showed comparative reactivity however a little higher yield was obtained using Cu-MCM-48.

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Synthesis of dithiocarbamates is important as they are valuable synthetic intermediates<sup>1</sup> and found in bio-active compounds.<sup>2</sup> Functionalized carbamates specially diarylalkyl thioureas are known to exhibit interesting medicinal and biological properties<sup>2</sup> and are used as non-vanilloid TRPV1 antagonists, possessing excellent therapeutic potentials in pain regulation<sup>3</sup> and human CB1 and CB2 cannabinoid receptor affinity.<sup>4</sup> For these reasons, the synthesis of dithiocarbamate derivatives with different substitution patterns at the thiol chain has become a field of increasing interest in synthetic organic chemistry during the past few years.

Several methods for the synthesis of dithiocarbamate derivatives have been reported in the literature, and among them, reactions of amines with costly and toxic reagents, such as thiophosgene and isothiocyanate, have been reported as the general routes.<sup>5</sup> Direct thiocarboxylation of amines with carbon monoxide and sulfur to form urea derivatives has been reported.<sup>6</sup> Recently, a one-pot reaction of amines with carbonyl sulfide, alkyl halides, or  $\alpha,\beta$ -unsaturated compounds also has been developed.<sup>7</sup> However, most of the above described methods have focused on the synthesis of alkyl dithiocarbamates and limited methods are present in the literature for the synthesis of aryl dithiocarbamates. Generally, these moieties have been prepared by the reactions sodium salt of dithiocarbamic acid,<sup>8</sup> or certain organometallic reagents with tetramethylthiuram disulfide.<sup>9</sup>

*S*-aryl-*N*-alkyl dithiocarbamate derivatives have been prepared by Bao *et al.*<sup>10</sup> *via* Ullmann-type coupling reaction of sodium dithiocarbamates with aryl iodides and vinyl bromides using CuI/*N*,*N*-dimethylglycine/K<sub>2</sub>CO<sub>3</sub> in DMF at 110 °C. However, longer reaction time (22 h), high temperature, and use of nitrogenous ligand are the major limitations of the protocol.<sup>10</sup> On the other hand, *N*-aryl dithiocarbamate derivatives have been synthesized by using  $\text{SnCl}_2^{11a}$  and basic  $\text{Al}_2\text{O}_3$  as catalyst.<sup>11b</sup> However, these methods required longer time (10-30 h), produced low isolated yields of products, and often made use of toxic reagents (*e.g.* SnCl<sub>2</sub>), harsh organic solvents such as DMF, DMSO and methanol <sup>10,11</sup> making these reactions laborious, timeintensive, and inefficient.

Thus, development of efficient and environment-friendly heterogeneous catalyst for the synthesis of biologically important *N*-aryl substituted dithiocarbamate derivatives is in great demand. However, heterogenization of homogeneous catalysts considerably decreases their catalytic efficiency by blocking the active sites of the catalysts. Thus, design and development of porous supports is essential for heterogenization of homogeneous catalysts. In this context, the development of mesoporous silica materials designated as  $M41S^{12}$  by Mobil Oil Corporation in 1992 enables one to tune the catalytic activity and selectivity of heterogeneous catalyst by changing their surface area and pore size. The pores in M41S class materials are uniform and are aligned in hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50) structures. The large surface area and narrow pore size distributions (tunable from 2 to 10 nm) make them an ideal support for catalytic reactions. Among the M41S class of materials, MCM-48 is interesting candidate as they possess relatively high surface areas (> 1000  $\text{m}^2\text{g}^{-1}$ ) which enables high dispersion of active sites of catalyst, good thermal stability, and finally, the interpenetrating network of three-dimensional pores, facilitate molecular transport of reactants and products more

efficiently compared to one-dimensional supports such as MCM-41.<sup>13</sup> On the other hand, SBA-15 an another well-known mesoporous silica sieve having uniform hexagonal pores with a narrow pore size distribution and larger pore diameter, which is also expected to enhance catalytic performance by assisting mass transport of reactant(s) and product(s).<sup>14</sup> Various transition metals in the form of metal or metal oxide have been incorporated into the framework positions in these mesoporous materials and/or have been dispersed onto the surface of siliceous mesoporous materials.<sup>15</sup> The idea behind this present work is that by dispersing catalytically active copper species on a high surface area mesoporous support with relatively large, uniform, and regular pores, one can realize high catalytic activity for the preparation of synthetically challenged *N*-aryl dithiocarbamate derivatives.

In this paper, we demonstrate the facile one-pot three component fabrication of synthetically challenging *N*-aryl substituted dithiocarbamate derivatives using mesoporous supported Cu-catalysts at room temperature in ethanol. Briefly, mesoporous, Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15 have been prepared by impregnation of Cu-salt on mesoporous materials and well-characterized by powder X-ray diffraction (XRD) and N<sub>2</sub> adsorption-desorption isotherms and transmission electron microscopic (TEM) studies and finally comparative studies have been performed for the synthesis of N-aryl-dithiocarbamate derivatives (Scheme 1).



**Scheme 1.** Synthesis of N-aryl-dithiocarbamate derivatives using Cu supported mesoporous materials.

Initially, we have synthesized Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15 by simple impregnation of Cu-salt onto the surface of pre-synthesized mesoporous silica materials followed by calcination following reported procedure.<sup>16-18</sup> The detailed experimental procedure for the preparation of Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15 are given in the supporting information. The structural and physico-chemical properties of the three materials were determined by powder XRD,  $N_2$  adsorption-desorption and transmission electron microscopic (TEM) studies.

The powder X-ray diffraction patterns (XRD) of the Cu-based mesoporous catalysts were recorded on a Rigaku Ultima IV X-ray diffractometer using Cu K $\alpha$  radiation of  $\lambda$ = 1.540806 Å. The diffractometer was operated at 40 kV and 40 mA and with a step width of 0.02° and the scan rate used was 0.24°/min.

The powder XRD studies (see Figure S1 in the supporting information) revealed that Cu-MCM-41 has diffraction peaks at  $2\theta = 2.3^{\circ}$ , and  $4.5^{\circ}$  due to (100) and (110) reflection planes respectively and the powder XRD pattern is consistent with MCM-41 type of materials.<sup>16</sup> The powder XRD pattern of Cu-MCM-48 is also similar to cubic MCM-48 reported by us previously<sup>17</sup> with the basal diffraction peaks at  $2\theta = 2.7^{\circ}$  and  $3.1^{\circ}$ , corresponding to (211) and (220) diffractions of the *Ia d* cubic structure.<sup>19</sup> The powder diffraction pattern of Cu-SBA-15

is indicated by the characteristic peaks at the (100), (110), and (200) reflections consistent with SBA-15 mesostructure.<sup>20</sup>

Therefore, the loading of Cu does not destroy the periodic mesoporous structure of the MCM-41, MCM-48, or SBA-15 support. The high-angle powder XRD experiments of the Cu-based mesoporous materials were also investigated and the results (not shown) indicate the presence of a very broad peak at  $2\theta$  near 25° which is due to the presence of the amorphous silica support. No other peaks were observed indicating that the copper species is highly dispersed on the high surface area support precluding its detection. Alternatively, it is also possible that the copper moieties are also in the amorphous form and hence are not detected. Thus, the powder XRD measurements indicate that the mesostructure is preserved on loading with Cu-species and that they are well dispersed on the mesoporous support.

Next, we have studied the N2 adsorption-desorption of materials to determine the physicochemical properties. The N<sub>2</sub> adsorption-desorption isotherms of the catalysts were performed using a Quantachrome Nova 2200e gas adsorption analyzer at 77K. Samples were dried in an air oven overnight and degassed at 100 °C extensively, prior to the adsorption measurements. The nitrogen adsorption/desorption isotherms of mesoporous Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15 were given in the supporting information. The surface area was determined using the Brunauer-Emmett-Teller (BET) equation in the relative pressure range of  $(P/P_0) = 0.05$  to 0.30. The pore sizes were calculated by applying the Barrett-Joyner-Halenda (BJH) equation to the desorption isotherm. The pore volume was calculated from the amount of nitrogen adsorbed at the highest pressure  $(P/P_0)$ 0.98. relative ~ The nitrogen adsorption/desorption isotherms the pore size distribution plots of the various Cu-based mesoporous catalysts were given in the supporting information (see Figure S2 and S3 in SI-2). Table 1 lists the surface area  $(S_{\text{BET}})$ , pore diameter (Dp) and total pore volume (Dv) of mesoporous Cu-catalysts.

As listed in Table 1, Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15 materials have surface areas of 954, 565, and 493  $m^2g^{-1}$  respectively. A steady increase in surface area was observed from SBA-15 to MCM-41.

**Table 1.** Physicochemical properties of Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15

Entry	Cu-catalyst	$S_{BET}$ (m <sup>2</sup> /g)	$D_{\rm v}$ (cm <sup>3</sup> /g)	D <sub>p</sub> (nm)
1	Cu-MCM-41	954	0.49	2.2
2	Cu-MCM-48	565	0.31	1.9
3	Cu-SBA-15	493	0.74	6.6

These materials have pore volumes (Dv) of 0.49, 0.31 and 0.74 cm<sup>3</sup>/g respectively whereas the pore diameters (Dp) were determined to be 2.2, 1.9, and 6.6 nm respectively. Thus, Cu-SBA-15 contains larger pore volumes and pore diameter (Table 1, entry 3).

Transmission electron spectroscopy (TEM) images were obtained using an FEI Tecnai  $G^2$  Spirit instrument at an acceleration voltage of 120 kV. TEM images were recorded by first sonicating a dispersion consisting of the mesoporous sample in ethanol and then by carefully placing a drop of the sonicated dispersion on a carbon-coated copper grid (mesh size = 200).

This was allowed to air dry overnight before transferring to the vacuum chamber of the TEM instrument. The transmission electron micrograph of a representative Cu-based mesoporous material (Cu-SBA-15) is shown in Figure 1. The well-ordered cylindrical pore geometry of the mesoporous SBA-15 support can be seen in the TEM image (Figure 1). The TEM images corresponding to Cu-MCM-41 and Cu-MCM-48 are given in the supporting information (see figure S4 and S5).



Figure 1. Transmission electron microscope image of mesoporous Cu-SBA-15.

The catalytic activity of the mesoporous Cu-materials were tested for the synthesis of aryldithiocarbamate derivatives and a three component reaction of aniline, CS<sub>2</sub>, and methyl acrylate has been chosen as a model reaction. When methyl acrylate (1.1) mmol) was added to a stirred solution of aniline (1 mmol), CS<sub>2</sub> (2.5 mmol) and Cu-materials (20 mg) in ethanol, excellent yields of products was observed. As reflected in Table 2, all three Cucatalysts produced good to excellent yields of products. However, Cu-MCM-48 provided a slightly higher yield of Nphenyl dithiocarbamate. The higher reactivity of Cu-MCM-48 is probably due to the three-dimensional interpenetrating network of pores in the cubic material that facilities enhanced molecular trafficking of reactants and products in comparison to the unidimensional nature of pores in MCM-41 and SBA-15 that is more prone to clogging effects. The non-doped catalyst, MCM-48 exhibited little activity and yielded 22 % of product after 12 hours stirring at room temperature (entry 4, Table 2).

NH <sub>2</sub> + (	CS <sub>2</sub> + CO <sub>2</sub> Me	Cu-catalyst Solvent	N H	S S CO <sub>2</sub> M
Entry	Catalyst	Solvent	Time (h)	Yield $(\%)^{a}$
1	Cu-MCM-41	EtOH	1	80
2	Cu-MCM-48	EtOH	1	95
3	Cu-SBA-15	EtOH	1	85
4	MCM-48	EtOH	12	22

Table 2. Study of catalytic activity of mesoporous Cu-materials

<sup>a</sup> Yields refer to those of pure isolated products.

Next, we have examined the effect of solvents in this reaction using Cu-MCM-48 catalyst and found that the catalysts showed highest reactivity in ethanol showing 95% yield of the product. Assuming that all the Cu moieties are active sites, the turnover rate for the conversion of aryl aniline as indicted in Table 2 for Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15 is calculated to be  $1.98 \times 10^3 \text{ h}^{-1}$ ,  $2.35 \times 10^3 \text{ h}^{-1}$ , and  $2.10 \times 10^3 \text{ h}^{-1}$  respectively indicating that the reactions are catalytic in nature. The reaction in EtOH-H<sub>2</sub>O (1:1) mixture also yielded impressive yields (90%). 20 mg of Cu-MCM-48 was sufficient for this conversion and increasing amount of catalyst did not increase the yield of the product.

 Table 3. Solvents effect of on Cu-MCM-48 catalyzed synthesis of methyl 3-((phenylcarbamothioyl)thio)propanoate.

PI	n-NH <sub>2</sub> + C	S <sub>2</sub> + CO <sub>2</sub> Me	Cu-MCM-48 Solvent	S PhHN S	∕CO₂Me
-	Entry	Cu-MCM-48	Solvent	Time (min.)	Yield <sup>a</sup> %)
	1	Cu-MCM-48	CH <sub>3</sub> CN	60	75
	2	Cu-MCM-48	EtOH	60	95
	3	Cu-MCM-48	$H_2O$	60	80
	4	Cu-MCM-48	EtOH:H <sub>2</sub> O (1:1)	60	90
	5	Cu-MCM-48	THF	60	35
1	6	Cu-MCM- 48 <sup>b</sup>	EtOH	60	96

Reaction Conditions: Aniline (1 mmol), CS2(2.5 mmol), methyl acrylate (1 mmol), Solvent (2 ml), 10% Cu-MCM-48 (20 mg), Stirring at room temparature. <sup>a</sup> Isolated yield, <sup>b</sup> 50 mg of 10% Cu-MCM-48 was used.

Using the optimized reaction conditions i.e. 20 mg of Cu-MCM-48 in ethanol at room temperature we have explored the scope for the synthesis of different N-aryl-S-substituted dithiocarbamate derivatives. In a simple experimental procedure,<sup>21</sup> aromatic amines (1 mmol) were treated with  $CS_2$  (2.5 mmol) in presence of Cu-MCM-48 (20 mg) in ethanol (1 ml) and stirred for 20 minutes at room temperature. After that different conjugated alkenes were added and stirred till completion of reaction (monitored by thin layer chromatography). The solid products were dissolved in hot ethanol and the catalyst was filtered, washed with ethanol, dried, and reused for subsequent reactions. The filtrate was kept at room temperature and crystals of dithiocarbamate derivatives appeared. The crystals were separated by filtration and washed with ethanol (2 x 1 ml) and dried in oven at 50 °C. The formation of products was confirmed by melting point determination and spectroscopic analysis. The melting points were in well-accordance with reported values and spectral data were also in good agreement with reported values in literature. The results for the mesoporous Cu-MCM-48 catalyzed synthesis of N-aryl dithiocarbamates have been presented in Table 4. It was observed that aniline and 4-methoxyaniline (containing an electron donating substituent) participated in three component reactions without any difficulty however; presence of a electron withdrawing substituent on the aniline aromatic ring (e.g. 4-nitroaniline) retarded the reactions resulting in lower yields of the products (entry 7, Table 4). This is due to the fact that lone pair of electron on nitrogen in case of 4-nitroaniline delocalized to nitro group (-R effect) via resonance and decreases the rate of reaction. On the other hand, electron donating nature of -OMe group (+R effect) accelerate the rate of reaction by increasing the electron density on nitrogen. The presence of

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methyl group at ortho position of aromatic amine dose not retards the rate of the reaction (entry 9, Table 4). However, when the same reaction was conducted with 2,6-dimethyl aniline, a significant decrease in yield was observed and only 65% product was obtained (entry 8, Table 4) In addition, the reaction using diphenyl amine was not successful and starting material was recovered even after 2 h stirring at room temperature. The slower rate with 2,6-dimethyl aniline and non-reactivity of diphenyl amine could be possibly due the steric hindrance at the reaction center. The reactions provide high yields within one hour.

Table 4. Synthesis of N-aryl dithiocarbamate derivatives using Cu-MCM-48.



Reaction Conditions: Aniline derivative (1 mmol), Carbon disulfide (2.5 mmol), Conjugated alkene (1 mmol), EtOH (2 ml), Cu-MCM-48 (20 mg), Stirring at room temperature <sup>a</sup>Isolated vield.

This present protocol for the synthesis of N-aryl substituted dithiocarbamates has several advantages over previously reported methods and a comparative result of catalytic performance of mesoporous Cu-materials with the reported catalysts for the synthesis of N-aryl dithiocarbamate derivatives has been presented in Table 5. The results in Table 5 clearly demonstrated the advantages of the present synthetic route using mesoporous Cu-materials in terms of the following criteria: (i) mild and neutral reaction conditions (room temperature), (ii) faster reaction (1.5 h) compared to reported methods<sup>11</sup> and (iii) high isolated yields of the products.

Table 5. Comparative results of catalysts for the synthesis of Naryl dithiocarbamate derivatives via one-pot three component reaction of aryl amine, CS2 and conjugated alkenes

Entry	Catalysts/Conditions	Time (h)	Yield (%)	Ref.
1	CuI/N,N- dimethylglycine/K <sub>2</sub> CO <sub>3</sub> in DMF/100 °C	22	75-95	10
2	SnCl <sub>2</sub>	2.5	89-95	11a
3	Basic Al <sub>2</sub> O <sub>3</sub>	10-30	30-93	11b
4	Mesoporous Cu-materials	0.5-1.5	65-96	Present work

The results in Table 5 clearly demonstrated the advantages of the present synthetic route using mesoporous Cu-materials in terms of the following criteria: (i) mild and neutral reaction conditions (room temperature), (ii) faster reaction (1.5 h) compared to reported methods<sup>11</sup> and (iii) high isolated yields of the products. With the advantageous just listed, the protocol using mesoporous Cu-materials fulfills the criteria for green synthesis.

#### Conclusion

In conclusion, mesoporous supported Cu-catalysts namely Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15 have been prepared by simple impregnation of Cu-salt to synthesized mesoporous materials and characterized by powder XRD, nitrogen adsorption-desorption, and TEM studies. The mesoporous supported Cu-catalysts have showed excellent catalytic performance for the construction of synthetically challenged and biologically important N-aryldithiocarbamate derivatives at room temperature under mild conditions. All three catalysts produced good to excellent yields of N-aryldithiocarbamate derivatives at room temperature and higher yield was obtained using Cu-MCM-48 catalyst. The higher reactivity for Cu-MCM-48 is probably due to the interpenetrating network of three-dimensional pores in the cubic material that facilities enhanced diffusion of reactants and products in comparison to the one-dimensional nature of pores in MCM-41 and SBA-15 that is more prone to clogging effects. The present protocol offers several advantages such as mild reaction conditions (room temperature), faster reaction (1 h), easy separation of catalyst from the reaction mixture, high isolated yields of the products (up to 95%) and environmentfriendly in nature.

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#### **Supplementary Material**

Experimental procedure for the preparation of Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15 materials, characterization data of Cu-Mesoporous materials such as Small-angle X-ray diffraction patterns of Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15 materials, adsorption/desorption isotherms nitrogen of

mesoporous Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15, pore size distribution of Cu-MCM-41, Cu-MCM-48, and Cu-SBA-15, TEM images of Cu-MCM-41, Cu-MCM-48 and copies of <sup>1</sup>H NMR spectra of *N*-aryl dithiocarbamate derivatives are available free of charge at www.sciencedirect.com.

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- 21. General procedure for the synthesis of dithiocarbamate derivatives using mesoporous-Cu catalyst: Representative experimental procedure for the synthesis of methyl 3-((phenylcarbamothioyl)thio)propanoate using Cu-MCM-48 as catalyst (entry 1, Table 4):

Methyl acrylate (86 mg, 1 mmol) was added in portion to a well stirred mixture of aniline (93 mg, 1 mmol), carbon disulfide (190 mg, 2. 5 mmol) and Cu-MCM-48 catalyst (20 mg) in ethanol (2 mL) and this mixture was continued to stir at room temperature till completion of reaction (TLC-monitored). The reaction mixture was extracted with ethyl acetate  $(3 \times 7 \text{ ml})$  and then the extract was washed with brine and dried over anhydrous Na2SO4. Evaporation of the solvent left the crude product which was purified by column chromatography to provide pure methyl 3-((phenylcarbamothioyl)thio)propanoate (242.6 mg, 95% yield) as yellowish solid. A similar protocol was followed for the synthesis of methyl 3-((phenylcarbamothioyl)thio)propanoate using three mesoporous Cu materials namely, Cu-MCM-41, Cu-MCM-48 and Cu-SBA-15. All the products listed in Table 4 were characterized by their melting point determination and <sup>1</sup>H NMR study. These values are in well accordance with the reported values.<sup>1</sup>