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Copper(I)-N_2S_2-salen type complex covalently anchored onto MCM-41 silica: an efficient and reusable catalyst for the A^3-coupling reaction toward propargylamines

Hossein Naeimi* and Mohsen Moradian

The immobilization of copper complexes by covalent anchoring of the ligand on the surface of mesoporous MCM-41 has been described. Bis[2-(phenylthio)benzylidene]-1,2-ethylenediamine as a new N_2S_2 donor salen-type ligand was covalently anchored onto nanopores of MCM-41 coordinated with copper (I) halide. The organic–inorganic hybrid material was achieved readily using 3-mercaptopropyltrimethoxysilane as a reactive surface modifier. 2-Nitrobenzaldehyde was reacted smoothly with the thiol moieties in order to form functionalized nanoporous silica with carbaldehyde groups. The resulting supported organic moieties were converted to thiosalen ligand and coordinated with CuX (X = CN, Cl, Br, I). Characterization of the heterogeneous catalyst by X-ray diffraction, N_2 sorption, FT-IR, diffuse reflectance UV-visible and TGA techniques indicated successful grafting of the copper complex inside the nano-channels of MCM-41. The heterogenized catalyst was evaluated by the Mannich condensation reaction of aldehydes, amines and alkynes. In this reaction, the corresponding propargylamines were obtained as single products in good to excellent yields. Factors such as reaction temperature, solvent, catalyst loading, leaching and reusability of the catalyst also were discussed. The use of MCM-41 as support permits an easier separation and recycles with only a marginal decrease in reactivity. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: thiosalen; copper(I); heterogeneous; MCM-41; catalyst; A^3-coupling; propargylamine

Introduction

The development of new mesoporous organic–inorganic hybrid materials, as an example of heterogeneous catalysts, has played a key role in eco-friendly industrial processes.[1,2] Producing side waste materials, difficulty in separating expensive catalysts and contamination of the catalyst in the product are the major drawbacks of homogeneous systems. Immobilization of metal organic complexes on solid supports is highly desirable due to the facilitation of both isolation and recycling of the catalyst by simple filtration. Moreover, these catalysts exhibit a significant improvement in activity, selectivity and stability, which are attributed to contributions of isolated sites on the solid surface.[3–5]

Efficient anchoring of a ligand to the ordered mesoporous silica MCM-41 via a covalent bond has become an often employed method of catalyst heterogenization.[6] Immobilization inside the pores makes the catalysts more thermally stable, with a high surface area, and prevents them from dimerization.[7]

Transition metal complex-catalyzed C-C bond formation reactions have received increasing attention during recent decades. The synthesis of propargylamines by a three-component Mannich-type reaction represents a highly attractive and powerful method in organic synthesis.[8–10] These compounds are key intermediates for synthesis of different types of nitrogen compounds and a structural potential of many pharmaceutically active compounds[11,12] and natural products.[11,13–15] Propargylamines can be prepared by an A^3-coupling reaction between aldimines and activated C-H of alkynes by a catalyst[16–19] such as copper(I) complex,[20] various copper halides[21] such as CuCl,[22] CuBr[23] and CuI,[24–26] or coordinated with organic donor ligands have been widely used as the most extensively utilized catalysts.[27] Recent reports in this field have included the development of recoverable and reusable catalysts through organic–inorganic hybrid materials.[28–30] Immobilizing the copper metal as an efficient catalyst in the reaction via silica supports,[31–33] molecular sieves,[34] magnetite,[35] zeolites[36] or Pybox complexes on polystyrene resin[37] and Cu(I)–MOF[38] as heterogeneous catalysts have also been reported.

This work describes our efforts in anchoring an copper(I) complex of thiosalen ligand as bis[2-(phenylthio)benzylidene]-cyclohexane-1,2-diamine (CuTS) into nano-channels of MCM-41 silica. The modified MCM-41 as a solid catalyst was used successfully in the C-H activation of alkynes on the Mannich-type reaction in the synthesis of propargylamines. The reaction does not require any co-catalyst and deactivation of the catalyst does not occur. For further consideration, we studied the minimum amounts of catalyst loading for the reaction. The stability and reusability of the catalyst after each trial were also investigated. Owing to the rich electron-donating nature of sulfur atoms, the thiosalen ligand increases stability of the copper(I) complex,

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improves catalytic activity and, using toluene as non-polar solvent, causes negligible leaching of copper from the catalyst.

Experimental

Material and Physical Measurements

All the solvents were purchased from Merck Co. (reagent grades) and were used as received unless otherwise specified. MCM-41 mesoporous silica material was purchased from Sigma Aldrich Co. as 643645-ALDRICH identity code and in powder form (4.5–4.8 nm unit cell size, 0.98 $cm^3\ g^{-1}$ pore volume, 2.5–2.7 nm pore size and ~1000 $m^2\ g^{-1}$ specific surface area). Infrared spectra were recorded as KBr pellets on a Nicolet FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer. X-ray diffraction (XRD) patterns were recorded by an X'PertPro (Philips) instrument with 1.54 Å wavelength X-ray beam and Cu anode material. Nitrogen adsorption measurements were performed at 77K using a Coulter Ofeisorb 100CX instrument. A Unicam 929 model flame atomic absorption spectrophotometer was used for copper determination. The atomic absorption spectrometer equipped with a copper hollow cathode lamp (lamp current 7.5 mA, wavelength 324.8 nm, spectral bandwidth 1.3 nm). A combination of hydrofluoric acid (5 ml) and nitric acid (5 ml) was used for total decomposition of the silica support (0.100 g) containing organic materials. Standard solutions of $CuSO_4.8H_2O$ were prepared by dilution of 1.0 mg ml^{-1} stock solution in a solution of 0.2 mol l^{-1} HNO_3.

Synthesis of Organo-functionalized MCM-41

Surface modification of MCM-41 silica with 3-mercaptopropyltrimethoxysilane (3-MPTMS) was carried out as follows. A 3.0 g sample of MCM-41 was placed in a round-bottom flask, dried at 110°C in an oven overnight in order to remove physically adsorbed water and cooled to room temperature. To the mixture of dried MCM-41 in 50 ml dry toluene, 2.0 g 3-MPTMS (10 mmol) as silane modifier was added and stirred under reflux conditions for 15 h. After completion of the reaction, the flask was cooled and the pure thio-functionalized MCM-41 material (MCM-RSH) was filtered on a sintered glass funnel, washed with toluene (3 × 10 ml) and dried under vacuum.

Synthesis of functionalized MCM-41 with carbaldehyde moiety

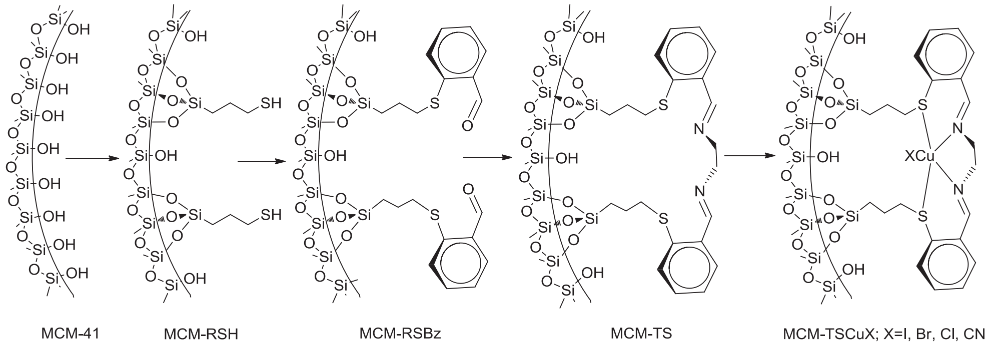
A suspension of MCM-RSH (3.0 g), 2-nitrobenzaldehyde (10 mmol, 1.50 g) and magnesium methoxide (20 mmol, 1.73 g) in 40 ml DMF was refluxed at 80°C for 15 h.[39] After cooling the resulting mass to 27°C, the solids were filtered, successively washed with acetone, dichloromethane, toluene and *n*-hexane and dried under vacuum. Due to the poisoning of the nano-channels of MCM-41 by irreversible pore blocking moieties, thorough washing of the heterogeneous catalyst is essential. The obtained material will be referred to as MCM-RSBz.

Synthesis of Anchored Thiosalen and Copper Complexes

The heterogeneous catalyst was obtained through the synthetic sequence as follows (Scheme 1). The MCM-RSBz was suspended in 50 ml methanol and ethylenediamine (10 mmol, 0.6 ml) in a suitable flask and refluxed for 12 h. After cooling the reaction mixture, the solid MCM-TS was collected by filtration, washed with methanol (3 × 10 ml) and dried under vacuum. Complexation of the MCM-TS was carried out in the presence of each of the $[Cu(MeCN)_4]X$ (X = Cl, Br, I, CN) solutions[40] as copper source in acetonitrile at 75°C and 15 h reaction time. The functionalized mesoporous MCM-41 was filtered and dried under vacuum, and the MCM-TSCuX catalyst was obtained.

General Procedure for the Synthesis of Propargylamines by the Solid Catalyst

The organic–inorganic hybrid material as catalyst was used for the preparation of propargylamines via A^3-coupling reaction of aldehydes, amines and alkynes. In a typical procedure, to a mixture of aldehyde (1.0 mmol), secondary amine (1.1 mmol) and alkyne (1.2 mmol) in toluene (10 ml) as solvent was added MCM-TSCuX as catalyst containing 3 mol% copper based on copper halide. The mixture was stirred at 80°C. After completion of the reaction (monitored by thin-layer chromatography), the resulting mixture was filtered on a sintered glass funnel and the solid catalyst washed with CH_2Cl_2 (3 × 5 ml) and methanol (3 × 5 ml). The filtrated was evaporated under reduced pressure to give the crude product as a viscous oil. The product was purified by column chromatography (10% EtOAc in hexane as eluent) to give the desired propargylamine. It should be noted that, in order to achieve reusability of the catalyst, thorough washing of the recovered heterogeneous catalyst is essential by using $CHCl_3$ (3 × 5 ml), absolute ethanol (3 × 5 ml) and finally THF (3 × 5 ml). This is on account of the poisoning of the mesoporous catalyst by irreversible pore blocking and reduction of yields in subsequent trials. Most of the compounds thus formed are known: propargylamines **a**,[33] **b**,[33] **d**,[31] **g**,[8] **h**,[33] **i**,[26,41] **j**,[8] **k**,[33] **l**,[33] **m**,[20,27] **n**,[42,43] **o**,[31] **p**[28] and **q**[44] have been previously reported. The unknown products, **e**, **c** and **f**



Scheme 1. Preparation of the modified MCM-41 silica.

(Fig. 5) were completely characterized by spectroscopic data as followed;

N,N-Dimethyl-4-(1-morpholino-3-phenylprop-2-yn-1-yl)aniline (**e**)

Red oil; IR (thin film): 2955, 2892, 2854, 2815, 1965, 1611, 1521, 115, 757, 692, 556. ^{1}H NMR (CDCl$_3$, 400 MHz): 2.65 (m, 4 H, H$_2$C-17, H$_2$C-21), 2.97 (s, 6 H, Me$_2$N-22), 3.73 (m, 4 H, H$_2$C-18, H$_2$C-20), 4.70 (s, 1 H, HC-7), 6.72 (d, $J = 8.4$ Hz, 2 H, HC-1, HC-3), 7.32 (m, 3H, HC-12, HC-14, HC-16), 7.45 (m, 2H, HC-13, HC-15), 7.50 (m, 2H, HC-4, HC-6). ^{13}C NMR (CDCl$_3$, 100 MHz): 44.11 (C-23, 24), 49.25 (C-7), 61.48 (C-17, 21), 68.03 (C-18, 20), 85.15 (C-10), 88.54 (C-9), 113.85 (C-1, 3), 120.41 (C-11), 123.74 (C-13, 15), 128.19 (C-14), 130.04 (C-5), 131.21 (C-12, 16), 134.30 (C-4, 6), 152.71 (C-2). MS: 320 ([M + 1]$^+$, 2.7), 215 (M+, 11), 276 (38), 234 (22), 219 (38), 101 (10), 86 (100), 76 (100). Anal. calcd for $C_{21}H_{24}N_2O$ (320.43): C 78.71, H 7.55, N 8.74; found: C 78.84, H 7.32, N 8.70.

*4-(1-(4-Nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**c**)*

Orange oil; IR (thin film): 3067, 2958, 2854, 2216, 1690, 1600, 1522, 1450, 1347, 1275, 1113, 1006, 864, 819, 757, 695, 539. ^{1}H NMR (CDCl$_3$, 400 MHz): 2.63–2.66 (m, 4 H, H$_2$C-16, H$_2$C-12), 3.76 (m, 4 H, H$_2$C-13, H$_2$C-15), 4.89 (s, 1 H, HC-7), 7.38 (s, 3 H, HC-21, HC-17, HC-19), 7.53 (m, 2H, HC-20, HC-18), 7.88 (m, 2H, HC-4, HC-6), 8.24 (m, 2H, HC-1, HC-3). ^{13}C NMR (CDCl$_3$, 100 MHz): 49.90 (C-7), 61.45 (C-12, 16), 67.04 (C-13, 15), 83.16 (C-10), 89.78 (C-9), 122.31 (C-20, 18), 123.48 (C-17, 19, 21), 128.45 (C-5), 128.72 (C-4, 6), 129.33 (C-11), 131.85 (C-1, 3), 145.45 (C-2). Anal. calcd for $C_{19}H_{18}N_2O_3$ (322): C 70.79, H 5.63, N 8.69; found: C 70.48, H 5.81, N 8.58.

*4-(1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine (**f**)*

Orange oil; IR (thin film): 3057, 2995, 2851, 2750, 1965, 1599, 1486, 1449, 1314, 1256, 1314, 1256, 1150, 1115, 1044, 1001, 867, 758, 692, 564. ^{1}H NMR (CDCl$_3$, 400 MHz): 2.66 (m, 4 H, H$_2$C-17, H$_2$C-21), 3.77 (m, 4 H, H$_2$C-18, H$_2$C-20), 3.85 (s, 3 H, H$_3$C-22), 4.79 (s, 1 H, HC-7), 6.87 (d, 8.3 Hz, 1 H, HC-2), 7.25–7.36 (m, 6 H, HC-1, HC-4, HC-6, HC-12, HC-14, HC-16), 7.53 (m, 2H, HC-13, HC-15). ^{13}C NMR (CDCl$_3$, 100 MHz): 49.99 (C-7), 55.24 (C-22), 62.01 (C-17, 21), 67.20 (C-18, 20), 85.15 (C-10), 88.54 (C-9), 113.10 (C-2), 114.39 (C-4), 120.99 (C-6), 123.03 (C-12, 16), 128.36 (C-14), 128.42 (C-5), 129.28 (C-13), 131.88 (C-15), 132.17 (C-11) , 139.57 (C-1), 159.71 (C-3). Anal. calcd for $C_{20}H_{21}NO_2$ (307): C 78.15, H 6.89, N 4.56; found: C 78.26, H 6.70, N 4.57.

Results and Discussion

Analysis of Catalysts

The heterogeneous modified MCM-41 with N_2S_2 thiosalen copper (I) complex was investigated by powder XRD, single-point N_2 adsorption–desorption method (BET), FT-IR, diffuse-reflectance UV-visible spectroscopy and TGA techniques. The results indicated successful anchoring of thiosalen complex to the internal surface of MCM-41 nanopores.

A comparison of the IR spectra of the catalyst with that of the initial mesoporous MCM-41 demonstrates the presence of organometallic complex anchored to the surface of nanopores (Fig. 1). The FT-IR spectrum of MCM-41 is dominated by some of the major mesoporous framework bands within the range 720–790 cm^{-1} ν_s (Si-O), 1020 cm^{-1} (Si-OH), 1130 cm^{-1} ν_{as} (Si-O) and 3550 cm^{-1} for isolated silanol (Si-OH) groups. These bands were detected in the functionalized material and supports that the functionalization process does not modify the MCM-41 structure. The IR spectra of the free ligand showed a strong band at 1614 cm^{-1} which was assigned to stretching vibration of the C=N group. This band shifts to a lower position by 6–9 cm^{-1} in complexes that suggests coordination of copper through C=N functional groups. For instance, in Fig. 1 we show the FT-IR spectra for thiosalen ligand (a), [Cu(TS)]I complex (b), MCM-41 (c), MCM-TS (d) and MCM-TSCuI (e).

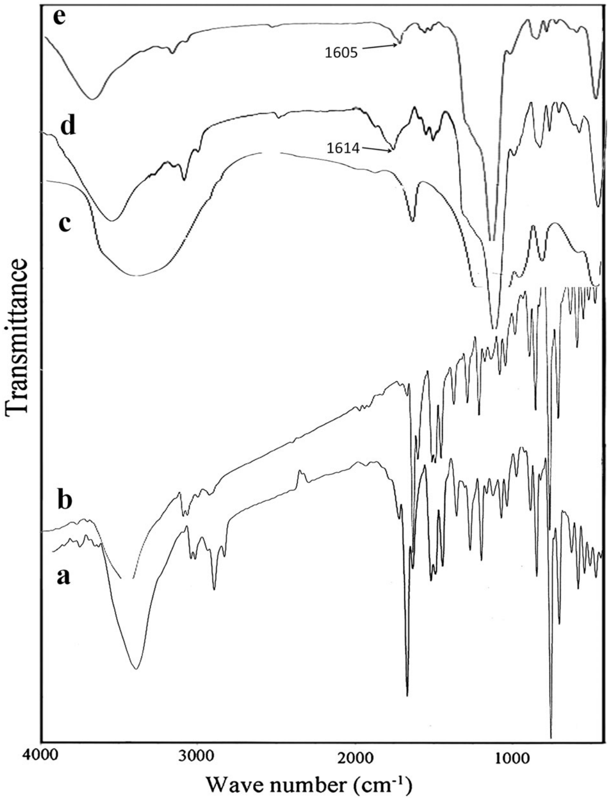


Figure 1. FT-IR spectra of thiosalen ligand (a), [Cu(TS)]I complex (b), MCM-41 (c), MCM-TS (d) and MCM-TSCuI (e).

The XRD pattern of MCM-41 typically demonstrates reflections between $2\theta = 2°$ and $5°$; since the materials are not crystalline at the atomic level, no reflections at higher angles are observed. The XRD pattern of modified mesoporous material with organo-copper complex is similar to that of untouched MCM-41 (Fig. 2), showing that the mesoporosity of the mesoporous material is retained.

The electronic spectra of thiosalen ligand were recorded in CH_2Cl_2 as solvent. The bands observed at 248 and 372 nm arise due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Since no $d \rightarrow d$ transitions are expected for d^{10} complexes, the UV-visible bands of the thiosalen copper complex at 454 nm are assigned to metal-to-ligand charge transfer (MLCT) or ligand-centered $\pi \rightarrow \pi^*$ transitions.[45,46] Comparison of UV-visible spectra for ligand, complex and functionalized mesoporous silica (diffuse reflective spectrum) confirms the presence of the anchored thiosalen complex (Table 1 and Fig. 3).

The single-point nitrogen sorption study for the functionalized MCM-41 silica shows that the specific surface area and pore volume are decreased. These results reasonably indicate that functionalization of Cu complex occurs inside the nano-channels of mesoporous MCM-41. The results on BET surface area and pore volume of MCM-41 and MCM-TSCuI are presented in Table 2.

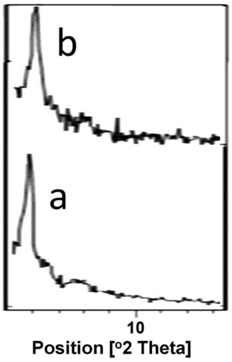


Figure 2. X-ray diffraction patterns of (a) MCM-41 and (b) MCM-TSCuI.

Sample	Conditions	Bands
N_2S_2-thiosalen	CH_2Cl_2	248, 372
[Cu(TS)]I	CH_3CN	264, 454
MCM-TSCuI	Solid	277, 436

Table 1. UV-visible and Diffraction Reflective Spectroscopy (DRS) absorption information of neat thiosalen ligand, [Cu(TS)]I complex and MCM-TSCuI

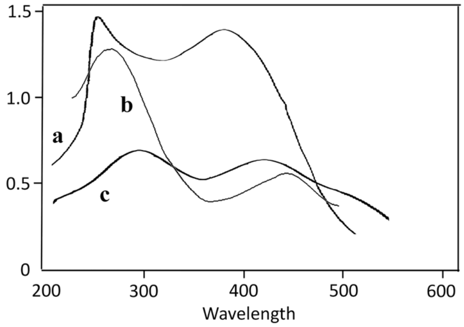


Figure 3. UV-visible spectra of N_2S_2-thiosalen ligand (a), $[Cu(N_2S_2)]I$ (b) and MCM-TSCuI (c).

Table 2. Specific surface area the MCM-41 and MCM-TSCuX getting from the single-point BET method

Sample	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
MCM-41	1000	0.98
MCM-TSCuI	330	0.51
MCM-TSCuBr	450	0.59
MCM-TSCuCl	494	0.62
MCM-TSCuCN	608	0.66

Thermal stability of the modified ordered mesoporous silica was studied by TGA. MCM-41 shows an endothermic weight loss in the range 50–140°C due to water physically adsorbed to the surface. The results of TGA for initial and modified silica are shown in Fig. 4. It is obvious that the TGA test shows continued weight loss of the solid support, which extends up to 590°C (Fig. 4). However, these results confirm that the copper complex was grafted into the nano-channels of MCM-41 silica.

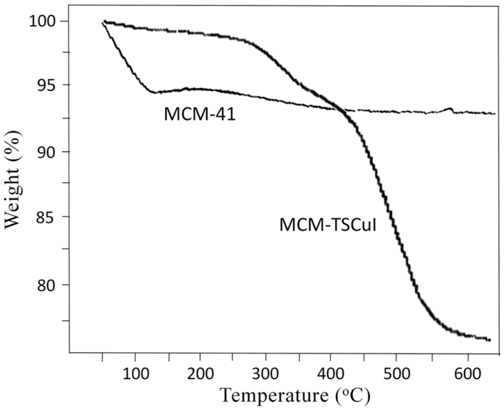


Figure 4. TGA and DTA of MCM-41 and MCM-TSCuI.

In order to analyze the copper in the solid modified silica, a known weight of each of the samples was destroyed in concentrated hydrochloric acid. The mixture was maintained at boiling temperature for 3 h on an oil bath. It was then cooled, diluted with water and filtered using ash-less filter paper, and was used for the estimation of copper in the encapsulated catalysts. The results of spectrophotometric determination of metal showed the amounts of copper that loaded in the surface of catalyst to be 0.084–0.098 mmol g^{-1} (Table 3). Figure 5

Catalytic Studies

The four heterogeneous and recoverable catalysts (MCM-TSCuX, X = Cl, Br, I, CN) were initially tested for A^3-coupling Mannich-type reaction of benzaldehyde, morpholine and phenylacetylene (Table 4, entries 3–6). The trials were carried out at various temperatures and catalyst loadings with toluene as solvent. According to Table 4, all catalysts exhibited moderate to high yields of propargylamine as unique product. However, comparison of these four species of solid catalysts confirms that MCM-TSCuI had a higher conversion of reaction than the other corresponding halides (Table 4, entry 6) and it was found to be the most effective one. In the presence of MCM-41, this reaction exhibited no products even after prolonged the reaction time under the same reaction conditions (Table 4, entry 2). However, no reaction occurred in the absence of any copper source as catalyst (Table 4, entry 1). Higher activity of functionalized mesoporous complexes was shown due to the site isolation of the copper halide in MCM-TSCuI as catalyst.

It is useful to mention here that, with 3 mol% catalyst based on copper(I) as the solid catalyst loaded in the reaction mixture, the reaction was generally completed in a reasonable number of hours (Table 4, entry 6). We also loaded different amounts of

Table 3. Determination of copper in the solid catalysts

Entry	Catalyst	Cu(I) (mmol g^{-1})[a]
1	MCM-TSCuI	0.084
2	MCM-TSCuBr	0.098
3	MCM-TSCuCl	0.089
4	MCM-TSCuCN	0.085

[a] Determined by atomic absorption spectroscopy.

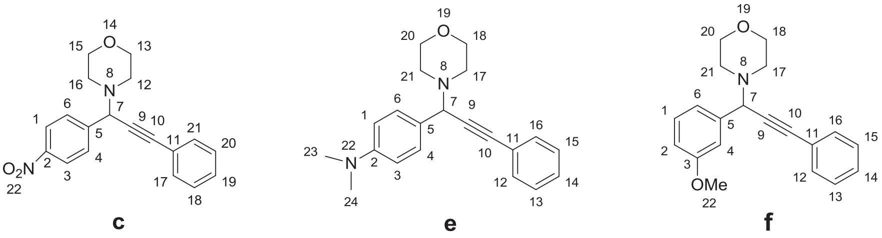
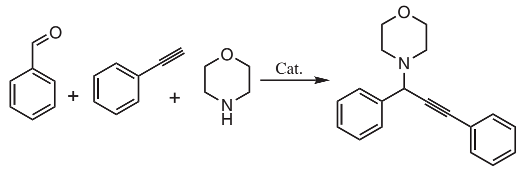


Figure 5. Structures of the new products.

Table 4. Search for optimal reaction conditions[a]



Entry	Catalyst (mol %)	Temp. (°C)	Time (h)	Yield (%)[b]
1	–	110	20	–
2	MCM-41	110	20	–
3	MCM-TSCuCN (3 mol %)	80	4	72
4	MCM-TSCuCl (3 mol %)	80	4	74
5	MCM-TSCuBr (3 mol %)	80	4	85
6	MCM-TSCuI (3 mol %)	80	4	92
7	MCM-TSCuI (3 mol %)	70	11	78
8	MCM-TSCuI (3 mol %)	50	16	72
9	MCM-TSCuI (3 mol %)	40	60	58
10	MCM-TSCuI (1 mol %)	80	25	35
11	MCM-TSCuI (5 mol %)	80	3	91
12	MCM-TSCuI (10 mol %)	80	3	92
13	Nonporous Silica-TSCuI	80	25	45

[a]Reaction conditions: benzaldehyde (1.00 mmol), phenylacetylene (1.20 mmol), morpholine (1.10 mmol), MCM-TSCuX as catalyst and $PhCH_3$ (5 ml) as solvent.

[b]Based on isolated yields.

Table 5. Solvent study in the A^3-coupling reaction toward propargylamine synthesis[a]

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	$PhCH_3$	80	4	92
2	DCE	70	5	72
3	CH_2Cl_2	40	20	55
4	$CHCl_3$	60	20	62
5	Cyc. hex.	70	10	18
6	MeOH	65	20	25
7	DMSO	80	8	77
8	MeCN	80	8	75
9	DMF	80	8	81

[a]Reaction conditions: benzaldehyde (1.00 mmol), phenylacetylene (1.20 mmol), morpholine (1.1 mmol), 360 mg heterogeneous MCM-TSCuI as catalyst that is equal to 0.03 mmol copper.

[b]Isolated yields based on benzaldehyde.

the selected catalyst in this reaction (Table 4, entries 10–12) in order to achieve optimization. Thus the optimized reaction conditions for catalyst loading and temperatures of the reaction were 3 mol% catalyst based on copper and 70°C, respectively.

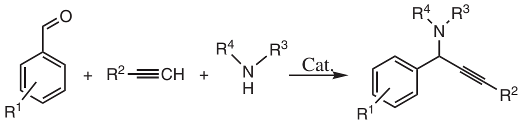
Solvents play an important role in this A^3-coupling Mannich-type reaction toward propargylamines. Various solvents were screened in this reaction in order to look for improved yields and more effective solvent (Table 4). With attention to the results shown in Table 5, toluene provided excellent yields and proved to be the solvent of choice. However, polar solvents such as DMSO, DMF and acetonitrile were found to be suitable for this reaction, with comparable yields (Table 5, entries 7–9), while leaching out of the copper ions from the pores of solid catalyst during the reaction makes these solvents unfavorable. The perfect mole ratio of aldehyde, amine and alkyne was found to be 1:1.1:1.2, respectively.

Investigation of the scope and generality of secondary amines, aldehydes and terminal alkynes applicable in the A^3-coupling reaction was attempted. The results are summarized in Table 6. It can be seen from these results that aromatic aldehydes with an electron-withdrawing group afforded high yields compared with an electron-donating group (Table 6, entries 3–6, 10). The coupling reaction proceeded readily and smoothly to provide the corresponding propargylamines in good to excellent yields by using various alkynes and amines, including aromatic and aliphatic substrates. Among the various amines studied, morpholine and piperidine as aliphatic amines gave higher yields than that aromatic phenylmethylamine. However, the dibenzylamine afforded a poor yield of the desired products. Aromatic alkynes and *n*-pentyne as aliphatic alkyne also underwent the corresponding coupling reaction smoothly and generated the products in excellent yields under the present reaction conditions.

It is well known that terminal alkynes can produce Glaser-type oxidative coupling products in the presence of copper salts and oxygen of air.[47] Whereas copper salts are used in this reaction, Glaser-type coupling could compete with the main reaction process and decrease yields of the propargylamines. Thus, to avoid this side product, it is necessary to work under an inert atmosphere and to use degassed solvents. However, because we did not observe any Glaser-type products using MCM-TSCuI as the catalyst, this reaction was performed in air atmosphere. Due to coordination of the copper metal in the N_2S_2 thiosalen donor ligand, the oxidation state of the metal strongly stabilizes, and copper is inactive for the Glaser-type coupling.

Furthermore, recyclability of the catalyst was studied because of the potential benefits in commercial applications. After the

Table 6. Formation of propargylamine compounds through three-component coupling reaction[a]

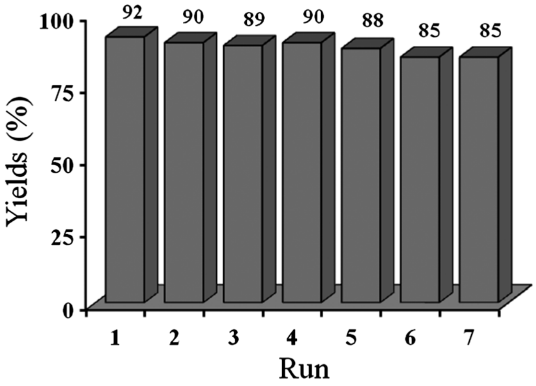


Entry	R^1	R^2	R^3, R^4	Product	Time (h)	Yield[b]
1	H	Ph	$O(CH_2\text{-}CH_2)_2$	**a**	4	92
2	*p*-CH_3	Ph	$O(CH_2\text{-}CH_2)_2$	**b**	5	91
3	*p*-NO_2	Ph	$O(CH_2\text{-}CH_2)_2$	**c**	4	93
4	*p*-OCH_3	Ph	$O(CH_2\text{-}CH_2)_2$	**d**	5	88
5	*p*-$N(CH_3)_2$	Ph	$O(CH_2\text{-}CH_2)_2$	**e**	7	83
6	*m*-OCH_3	Ph	$O(CH_2\text{-}CH_2)_2$	**f**	7	85
7	*p*-$CH(Me_2)$	Ph	$O(CH_2\text{-}CH_2)_2$	**g**	6	89
8	*o*-Cl	Ph	$O(CH_2\text{-}CH_2)_2$	**h**	8	87
9	*p*-Cl	Ph	$O(CH_2\text{-}CH_2)_2$	**i**	10	91
10	*m*-NO_2	Ph	$O(CH_2\text{-}CH_2)_2$	**j**	6	91
11	H	Ph	$(CH_2)_5$	**k**	5	88
12	*m*-CH_3	Ph	$(CH_2)_5$	**l**	8	85
13	H	Ph	$R^3 = -CH_3$ $R^4 = -Ph$	**m**	10	81
14	H	*n*-C_6H_{13}	$(CH_2)_5$	**n**	5	84
15	H	*p*-$CH_3C_6H_4$	$O(CH_2\text{-}CH_2)_2$	**o**	5	87
16	*p*-OCH_3	Ph	$(CH_2)_5$	**p**	6	86
17	*p*-CH_3	Ph	$(CH_2)_5$	**q**	9	83
18	*p*-CH_3	*n*-C_4H_9	R^3, $R^4 = -CH_2Ph$	**r**	9	83

[a] Aldehyde (1.0 mmol), alkyne (1.20 mmol), secondary amine (1.1 mmol), MCM-TSCuI as modified solid catalyst (350 mg, contains 0.03 mmol of Cu) in $PhCH_3$ (5 ml) at 80°C.

[b] Isolated yields based on aldehyde.

end of reaction, MCM-TSCuI solid catalyst was separated by filtration of the reaction mixture and was used in the coupling reaction of benzaldehyde, morpholine and phenylacetylene seven times. The corresponding results are depicted in Scheme 2. As can be seen, the solid catalyst can catalyze the reaction in at least seven consecutive runs without loss of activity. Also, the reaction in the non-polar solvent reduces leaching of the copper ions and increases recycling ability.



Scheme 2. Recycles of the heterogeneous MCM-TSCuI as recoverable catalyst for the A^3-coupling reaction.

Conclusion

In this research, complexes of the functionalized MCM-41 with Cu (I)-thiosalen were prepared and characterized to verify the structural and chemical properties by different chemical and physical analysis methods. It was shown that the novel N_2S_2 donor salen-type ligand can be readily grafted into the nanopores of MCM-41 silica. The ligand was strongly coordinated with copper(I) halides due to the soft donor atoms in their structure. The prepared MCM-TSCuI silica was applied as the most effective heterogeneous catalyst in the A^3-coupling reaction toward synthesis of propargylamines. The products were obtained in high to excellent yields and appropriate times, and the catalyst could be easily recovered and reused several times. Furthermore, over several cycles with toluene as solvent, catalyst activity was maintained without any significant loss of its activity.

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