FULL PAPER

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A novel heterogeneous nanocatalyst: 2-Methoxy-1-phenylethanone functionalized MCM-41 supported Cu(II) complex for C-S coupling of aryl halides with thiourea

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An environmentally friendly copper-based catalyst supported on 2-Methoxy-1-phenylethanone functionalized MCM-41 was prepared and characterized by FT-IR, FE-SEM, TEM, XRD, EDX, BET and ICP techniques. The catalyst was applied for the C−S cross-coupling reaction of aryl halides with thiourea. Corresponding products were produced in good yields in aerobic conditions. The catalyst could be recovered and recycled for several times.

KEYWORDS
Copper(II) catalyst, C-S coupling, heterogeneous, MCM-41, thiourea

1 | INTRODUCTION

Today, the C-S bond creation reactions are very important instruments in organic synthesis. Their significance is seen in making various arrangements of target compounds including pharmaceutical to biological molecules as well as for the expansion of novel precursors in the materials science and organic synthesis.[1,2] Various drugs, which are used for the cure of some diseases such as Parkinson, Diabete and Alzheimer, as well as HIV, inflammatory and microbial diseases, have aryl sulfide derivatives in their structures.[3–6]

Hence, researches in this field of science are moving further towards economical, efficient and eco-friendly methods and cheap and safe resources for C−S bond generation. In recent years, numerous cross-coupling reactions to create C-S bonds have been developed by transition metal catalysts including palladium,[7] cobalt,[8] nickel,[9] indium,[10] copper[11] and iron salts.[12–14]

Although these efforts have had some advantages such as high yields of corresponding products, C−S bond generation suffer from serious drawbacks including unstable, air sensitive and toxic thiols that can operate as transition metal catalyst poisons, using homogeneous catalysts that cannot be separated and recovered simply, toxic and expensive organic solvent, expensive ligandes and long time for completion the reaction, which can restrict the use of these reactions in the industry.[15,16]

To obviate these problems, many stable, inexpensive, low-toxicity and odorless sulfuration agents have been used as the sulfur source.[17–20] Among them, the non-toxic and odorless thiourea[21–29] is extensively used as

sulfur source that has been utilized in different transformations for producing the C−S bonds.

Moreover the metal nanoparticles grafted onto supports are more effective because of unmatched one-, two- or three- dimentional morphological properties and high surface to volume ratio compared with the catalysts based on accumulated metal particles.[30,31]

For these merits, immobilization of a homogeneous catalytic position on diverse supports such as zeolites,[32] magnetic materials,[33] carbon nanotubes,[34] chitosan,[35] alumina[36] and mesoporous materials[37–41] have created remarkable interest because of their essential, significant and green roles in transition metal catalyzed reactions.

The select of a support for catalyst mainly depends on the pore size and surface area of the support. The discovery of mesoporous material such as MCM-41 has made a stimulating option for immobilizing homogeneous catalysts and production of heterogeneous catalysts.[42] MCM-41 has extra-large surface area and large pore volume with abundant silanol groups that provide high numbers of the active sites for organic reactants.[43] However, pure MCM-41 demonstrated a finite catalytic activity due to the hydrophilic features and limited application. Therefore, it requires modification with organic functionalized groups to show other properties into mesoporous

silicates to improve their adsorption and hydrophobicity properties and active sites and formation of metal complexes by grafting an appropriate ligand to become as donor ligand for ions of transition metal.[44]

Up to the present time, some functionalized MCM-41-immobilized copper complexes have been synthesized and successfully used in different organic reactions.[45–54] It was demonstrated that the stability and activity of copper-based nanocatalysts is meaningfully enhanced after their formation on MCM-41.

To the best of our knowledge, a few examples describing the C-S coupling reaction of aryl halides and thiourea with MCM-41-supported copper heterogeneous systems and this subject still represents an actual challenge.

Herein, we reported 2-Methoxy-1-phenylethanone-Functionalized MCM-41 supported Cu(II) complex (Scheme 1) for synthesis of symmetric diaryl thioethers from different aryl halides with thiourea in the presence of K_2CO_3 base in water at 100 °C.
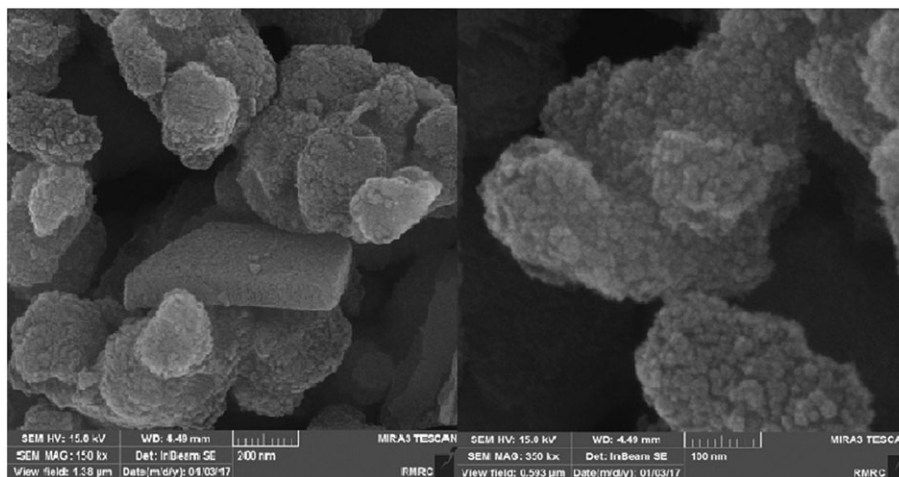
2 | RESULT AND DISCUSSION

2-Methoxy-1-phenylethanone functionalized MCM-41 supported Cu(II) complex [Cu(II)-2-MPE@MCM-41]
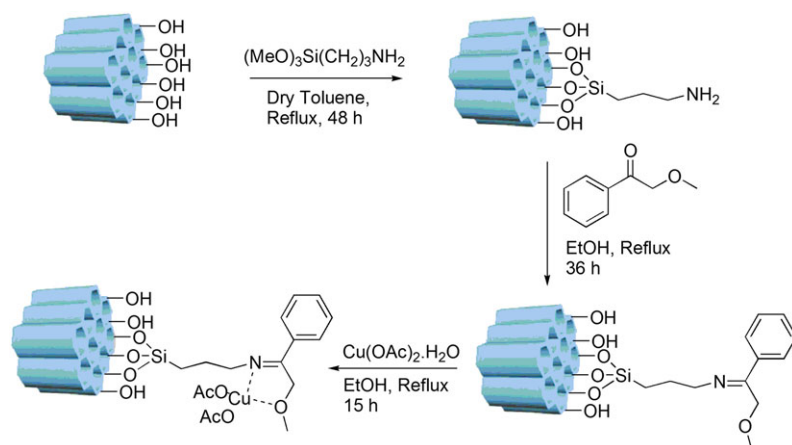
SCHEME 1 Preparation of Cu(II)-2-MPE@MCM-41 catalyst
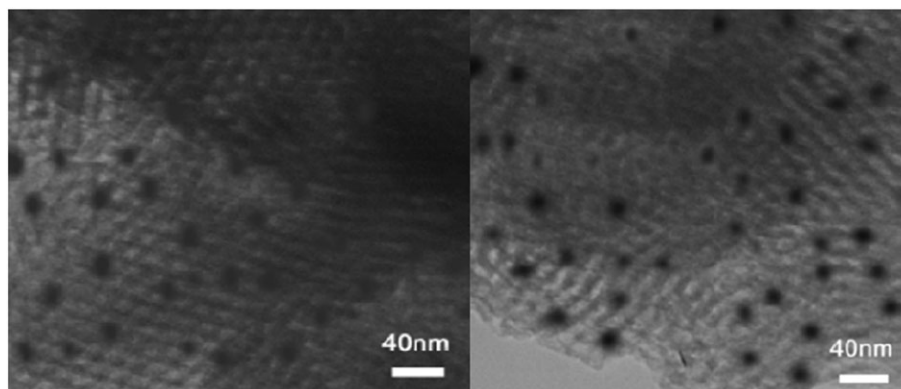
FIGURE 1 FE-SEM images of Cu(II)-2-MPE@MCM-41 catalyst

FIGURE 2 TEM images of Cu(II)-2-MPE@MCM-41 catalyst

TABLE 1 Textural characteristics of MCM-41 and Cu(II)-2-MPE@MCM-41

No	Sample	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
1	MCM-41	971.063	1.407	2.5
2	Cu(II)-2-MPE@MCM-41	401.910	0.710	1.33

TABLE 2 Optimization of the Cu(II)-2-MPE@MCM catalyzed coupling of 4-methoxy iodobenzene with thiourea under various conditions[a]

Entry	Cat (mmol Cu)	Solvent	Base (eq)	$T\ (^o C)$	Time (h)	Yield[b] (%)
1	2-MPE@MCM-41	DMSO	KOH (2)	130	12	-
2	Cu(II)-2-MPE@MCM-41 (0.15)	DMSO	KOH (2)	130	12	65
3	Cu(II)-2-MPE@MCM-41 (0.15)	DMF	KOH (2)	130	12	71
4	Cu(II)-2-MPE@MCM-41 (0.15)	NMP	KOH (2)	130	12	62
5	Cu(II)-2-MPE@MCM-41 (0.15)	H_2O	KOH (2)	130	12	60
6	Cu(II)-2-MPE@MCM-41 (0.15)	EtOH	KOH (2)	130	12	53
7	Cu(II)-2-MPE@MCM-41 (0.15)	EtOH:H_2O (1:1)	KOH (2)	130	12	66
8	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	KOH (2)	130	12	75
9	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	K_2CO_3 (2)	130	12	61
10	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	Na_2CO_3 (2)	130	12	64
11	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	K_3PO_4 (2)	130	12	69
12	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	KOH (3)	130	12	82
13	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	KOH (4)	130	12	82
14	Cu(II)-2-MPE@MCM-41 (0.15)	DMF:H_2O (1:1)	KOH (3)	140	12	82
15	Cu(II)-2-MPE@MCM-41 (0.10)	DMF:H_2O (1:1)	KOH (3)	130	12	82
16	Cu(II)-2-MPE@MCM-41 (0.07)	DMF:H_2O (1:1)	KOH (3)	130	12	63
17	Cu(II)-2-MPE@MCM-41 (0.10)	DMF:H_2O (1:1)	KOH (3)	130	14	82

[a]Reaction conditions: 4-methoxyiodobenzene (2 mmol), thiourea (1 mmol), Cu(II)-2-MPE@MCM, base, solvent (4 ml).

[b]Isolated yield.

was prepared according to Scheme 1. First, 3-Aminopropyltrimethoxysilane reacted with pure MCM-41 in dry toluene as a solvent. Then, the modified MCM-41 reacted with 2-Methoxy-1-phenylethanone in acetonitrile to achieve the 2-MPE@MCM-41. The immobilization process of Cu^{2+} onto the 2-MPE@MCM-41 was done in the absolute ethanol according to the common techniques to obtain Cu(II)-2-MPE@MCM-41 catalyst.

Catalyst has been characterized by infrared analysis (FT-IR), X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) and BET.

FT-IR of the pure MCM-41 powder (Figure S1 in supporting information) clearly showed absorption bands of O–H groups at 3375 cm^{-1}, Si–O asymmetric stretching vibrations at 1100 cm^{-1}, Si–O symmetric stretching vibrations at 807 cm^{-1} and Si–O bending vibrations at 455 cm^{-1}. After loading of 2-Methoxy-1-phenylethanone on MCM-41 surface, new absorption peaks appeared at 3030 cm^{-1} (=CH stretching), 1650 cm^{-1} (C=N and C=C stretching) and 1465 cm^{-1} (C=C stretching) which confirm the synthesis of 2-MPE@MCM-41.

The XRD pattern of 2-Methoxy-1-phenylethanone functionalized MCM-41 supported Cu(II) complex is shown in Figure S2, The relating signals to the Cu(II) complex were detected by XRD. Also presence of copper in complex was acknowledged by the EDX analysis (Figure S3). The amount of copper incorporated into the 2-Methoxy-1-phenylethanone functionalized MCM-41 was determined by inductively coupled plasma (ICP), which showed a value of 0.85 mmol/g of the heterogenized catalyst.

The FE-SEM images showed the phase morphology of in the heterogeneous catalyst (Figure 1). TEM images of

TABLE 3 Scope of the reaction of aryl halides with thiourea, catalyzed by Cu(II)-2-MPE@MCM nanocatalyst[a]

Entry	Y	X	Time (h)	Yield[b] (%)
1	H	I	12	85
2	H	Br	16	84
3	H	Cl	24	81
4	4-NO$_2$	I	12	95
5	4-NO$_2$	Br	16	90
6	4-NO$_2$	Cl	24	90
7	2-NO$_2$	I	12	92
8	2-NO$_2$	Br	16	89
9	4-COCH$_3$	I	12	94
10	4-COCH$_3$	Br	16	92
11	3-COCH$_3$	I	12	91
12	3-COCH$_3$	Br	16	90
13	4-Cl	I	12	79
14	4-Cl	Br	16	77
15	4-CH$_3$	I	12	89
16	4-CH$_3$	Br	16	88
17	4-OCH$_3$	I	12	82
18	4-OCH$_3$	Br	16	78
19	4-OCH$_3$	Cl	24	79
20	4-NH$_2$	I	12	75
21	4-NH$_2$	Br	16	67
22	4-NH$_2$	Cl	24	60

[a]Reaction conditions: aryl halide (2 mmol), thiourea (1 mmol), Cu(II)-2-MPE@MCM (0.10 mmol Cu), KOH (3 eq), DMF:H$_2$O 1:1 (4 mL) and 130 °C.
[b]Isolated yield.

catalyst demonstrated uniform distribution and nano-sized Cu(II) particles in the polymer matrix. As a result, black spherical shapes and clear parts respectively show nanoparticles and MCM-41 (Figure 2). Also the histogram of the catalyst presente the distribution of Cu(II) particles in the nano range (Figure S4).

N_2 adsorption-desorption isotherms and the textural characteristics (BET surface area, average pore size and pore volume) of MCM-41 and Cu^{2+}-2-MPE@MCM-41 catalyst are indicated in Figure S5, Figure S6 and Table 1. Decrease in S_{BET}, V_P and d_P for Cu^{2+}-2-MPE@MCM-41 catalyst could be ascribed to the fixing of Cu^{2+} and modification on the surface MCM-41, which causes increase in the wall thickness and the possession of copper in the hexagonal pores.

Reactivity of 2-Methoxy-1-phenylethanone functionalized MCM-41 supported Cu(II) complex was investigated in the C−S coupling reaction of aryl halides with thiourea under aerobic conditions. The solvents, bases, temperatures, the amounts of the catalyst and time were varied in the experiments. The results show that these parameters are important to the outcome of the reaction (Table 2).

To obtain information on the optimal catalyst conditions, at the first we tested 2-MPE@MCM-41 (Table 2, entry 1) as catalyst, which has shown no ability to carry out the reaction. Then, we carried out our investigations to identify the best solvent for this reaction. Among the various solvents screened, in some solvents including DMSO, DMF, NMP, EtOH, H_2O, EtOH:H_2O and DMF:H_2O, the mixture of DMF:H_2O (1:1) was shown
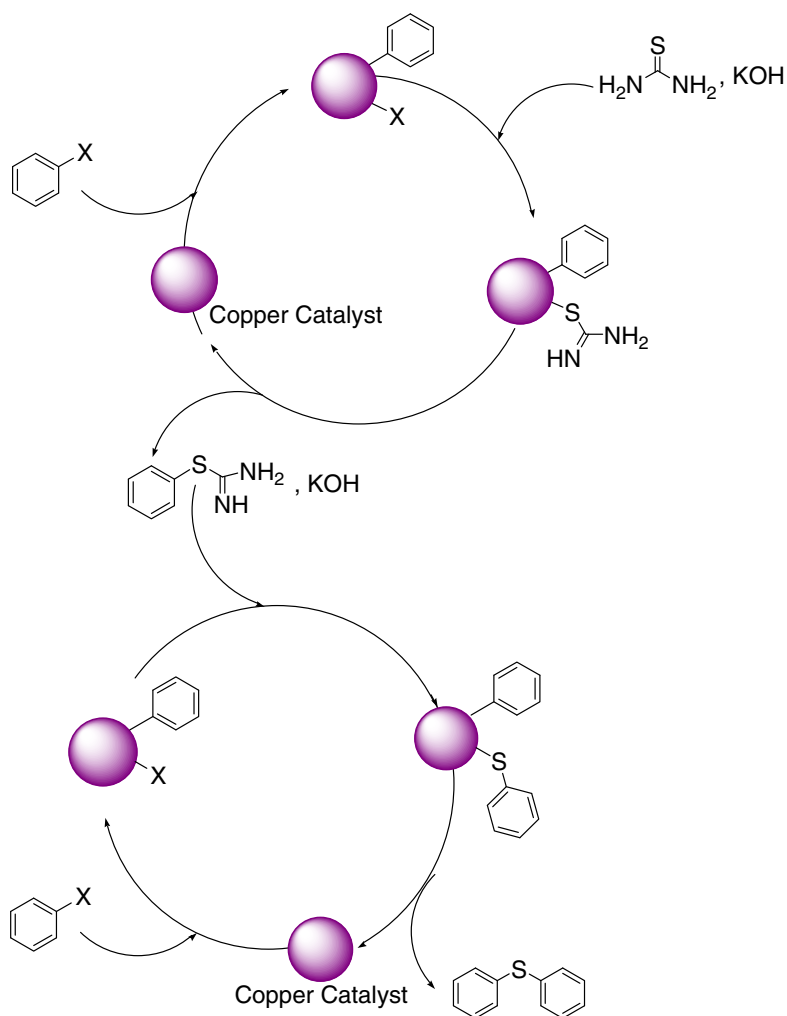
SCHEME 2 Proposed mechanism for synthesis of diaryl thioethers by thiourea

TABLE 4 Reusability of Cu(II)-2-MPE@MCM nanocatalyst in the reaction of 4-methoxy iodobenzene and thiourea[a]

Cycle	Fresh	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Yield[b] (%)	82	82	82	80	78	75	73

[a]Reaction conditions: 4-methoxyiodobenzene (2 mmol), thiourea (1 mmol), Cu(II)-2-MPE@MCM (0.10 mmol Cu), KOH (3 eq), DMF:H_2O 1:1 (4 ml) and 130 °C.

[b]Isolated yield.

to be the best solvent for this transformation (Table 2 entries 2-8).

The presence of the base is also essential to the C−S coupling reaction. Hence, some bases were checked for this transformation and KOH was specified to be the most efficient (Table 2, entries 8-11). 3 equivalent of KOH resulted in the best yield in 12 h at 130 °C (Table 2 entries 8, 12 and 13). Then we raised the temperature of reaction and found 130 °C is the best temperature (Table 2, entries 12 and 14). 0.10 mmol Cu resulted in the best yield in 12 h at 130 °C (Table 2, entries 15 and 16). Also we investigated the yield of reaction in 14 h and found that more time was not necessary (Table 2, entry 17).

These optimized reaction conditions were applied in the C−S coupling reaction for a variety of aryl iodide and bromides with thiourea. The results are summarized in Table 3.

When aryl iodide with electron-donating groups or electron-withdrawing groups were reacted with thiourea under the optimized conditions, the reactions proceeded well to produce the corresponding symmetric thioethers in good yields (Table 3, entries 1, 4, 7, 9, 11, 13, 15, 17 and 20). Thioetherification of different aryl bromides bearing either electron- withdrawing groups or electron-donating groups were carried out using thiourea in four hours longer and produced different diaryl thioethers (Table 3, entries 2, 5, 8, 10, 12, 14, 16, 18 and 21) in good yields. Also aryl chlorides were performed this reaction under optimum conditions in 24 hours and produced corresponding products in acceptable yields (Table 3, entries 3, 6, 19 and 22).

It seems the substituent effects in the aryl halides are important in this transformation. However, aryl halides with electron-withdrawing groups (such as NO_2 and $COCH_3$) had more yields than aryl halides with electron-donating groups (such as OCH_3).

Also, we propose a mechanism for C-S coupling of aryl halides with thiourea as shown in Scheme 2. At first, aryl halide connects to the catalyst and acetate ions leave. In the next step, thiourea ion replaces halide ion on the catalyst and 2-phenylisothiourea is produced as the first cycle product. Then this product goes into the next cycle. Second aryl halide adds to the catalyst and then the product of this cycle (diphenyl thioether) is obtained through an elimination step and the catalyst enters the next cycle.

We have also studied the recycling and reusability of our catalyst utilizing the reaction of 4-methoxy iodobenzene with thiourea under optimum conditions as the model reaction (Table 4).

After each run, the catalyst was recovered by filtration, followed by washing with water and ethyl acetate and then was dried. The activity of the catalyst remained almost fixed after it was reused six times. Also

a hot-filtration test was conducted using 4-methoxy iodobenzene with thiourea under optimum conditions. The solid catalyst was removed from the solution after 6 h reaction (~50% conversion) and the filtrate was carried out for another 6 h. After this time, no further improvement in product yield was detected upon catalyst removal. The characterization of recovered Cu(II)-2-MPE@MCM-41 was performed by XRD. The XRD pattern of recovered catalyst after sixth run was in compliance with the XRD pattern of fresh catalyst (Figure S2-b). As well, the obtained ICP result did not showed any copper into solution during the course of the reaction, indicating that the catalyst was truly heterogeneous in nature.

3 | CONCLUSION

In conclusion, We successfully prepared the 2-Methoxy-1-phenylethanone functionalized MCM-41 supported Cu(II) complex and developed an efficient procedure for the thioetherification of different aryl halides with thiourea and to provide the corresponding symmetrical diaryl sulfides in good yields and with a broad range of functional group acceptance. This catalyst could be simply recovered by simple filtration and reused for six times without an important loss in its activity and could proceed this reaction without expensive metal and toxic thiols.

4 | EXPRIMENTAL

4.1 | General

All chemical reagents were purchased from Merck or Fluka and were used without purification. FT-IR spectra were obtained as KBr pellets on a JASCO 680- Plus spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with $CDCl_3$ as solvent. Chemical shifts were measured in ppm using tetramethylsilane as an internal standard. Scanning electron microscope (SEM) images were performed using a Philips XL20 microscope. Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope. X-ray diffraction (XRD) powder patterns were obtained using an X′PERT MPD, with Cu Kα radiation (40 kV, 30 mA). BET analysis was taken with Specific Surface Area and Porosity Analyzer PHS-1020 (PHSCHINA). The amount of copper loading of the catalyst was obtained by ICP-OES using an Optima 7300 V ICP-OES spectrometer (PerkinElmer) and the EDX analysis (SEM, MIRA3 TESCAN) was engaged for characterization of the catalyst. Also, GC–MS was conducted using an Agilent 7890A-5975C instrument. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

4.2 | General Procedure for the synthesis of MCM-41 modified by 2-Methoxy-1-phenylethanone (2-MPE@MCM-41)

MCM-41 was prepared according to the process as described in a literature.[55] Initially, MCM-41 (2 g) was added into a suspension of 3-Aminopropyltrimethoxysilane (0.9 ml, 5 mmol) in dry toluene, and the reaction mixture was stirred at reflux for 48 h under N_2 gas. After cooling, solid was isolated from the solvent by filtration and washed with toluene and CH_2CL_2 (4 × 15 ml) and dried in vacuum at 140 °C for 5 h. The dried white solid was suspended in a solution of 2-Methoxy-1-phenylethanone (1.35 ml, 10 mmol) in ethanol (20 ml). The mixture was refluxed for 24 h under N_2 gas. After cooling, the reaction mixture was filtered and washed several times with ethanol and dichloromethane and dried in vacuum to afford 2-MPE@SiO2.

4.3 | General procedure for synthesis of Cu(II)-2-MPE@MCM-41

The obtained 2-MPE@MCM-41 was dispersed in 15 ml ethanol and a solution of $Cu(OAC)_2.H_2O$ (2 mmol) was added dropwise into this mixture under stirring and was refluxed for about 15 h. Next, the solid product was separated by filtration and washed with ethanol and acetone and dried in room temprature.

4.4 | General procedure for C—S coupling reaction by Cu(II)-2-MPE@MCM-41

A mixture of aryl halide (2.0 mmol), thiourea (1.0 mmol), KOH (3.0 mmol), Cu(II)-2-MPE@MCM-41 (0.10 mmol Cu) and 4 ml of $DMF:H_2O$ in a round bottom flask equipped with a condenser was stirred at 130 °C under air for 12 h (for aryl iodide). The reaction progress was controlled by the TLC. After completion of the reaction, catalyst was removed by filtration. Then, separated nanocatalyst washed by ethyl acetate and water, dried under vacuum at 60 °C and reused for next runs. Then the filtrate was extracted with ethyl acetate and the organic layer was dried over $CaCl_2$. The solvent was removed under vacuum, and the purified product was separated by silica gel column chromatography (n-hexane:EtOAc, 9:1).

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Data associated with this article contain FT-IR, histogram of nanocatalyst, EDX spectrum and XRD patterns, N_2 adsorption-desorption isotherms and spectral data of products can be found in the online version,