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Highly Efficient Oxidative Coupling of Thiols and Oxidation of Sulfides in the Presence of MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg as Novel and Recoverable Nanocatalysts

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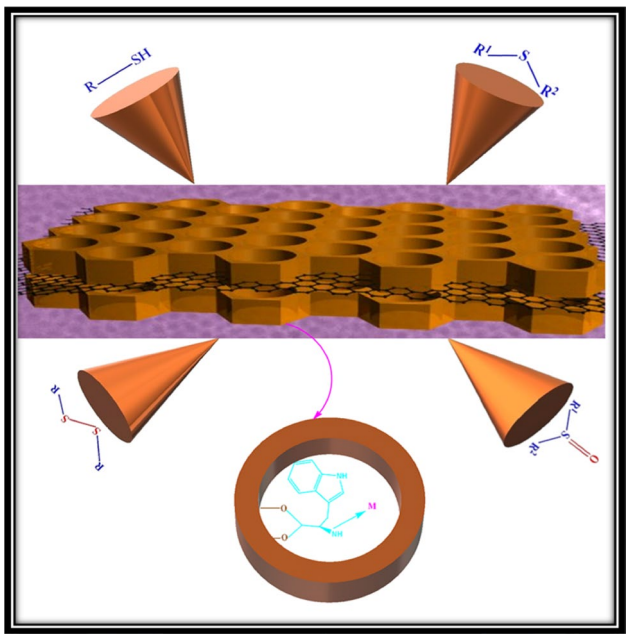
Abstract

Two heterogeneous catalysts, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg, were synthesized by immobilization of Cd or Hg complexes on MCM-41 as novel, efficient, recoverable and stable nanocatalysts for Oxidation of sulfides to sulfoxides and oxidative coupling of thiols into their corresponding disulfides. These functionalized complexes were characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and N_2 adsorption–desorption isotherms. The designed catalysts successfully oxidized a variety of sulfides and thiols with short reaction times in high to excellent yields at room temperature and recovered for several times without significant loss of their catalytic activity.

Graphical Abstract

Synthesis of Cd and Hg tryptophan complexes immobilized on to surface of mesoporous MCM-41 under mild reaction conditions has been presented. After characterization of these catalysts, their catalytic activity has been investigated for the synthesis of sulfoxide and disulfides derivatives.



Keywords MCM-41 · Heterogeneous catalysts · Sulfoxide and disulfides

Extended author information available on the last page of the article

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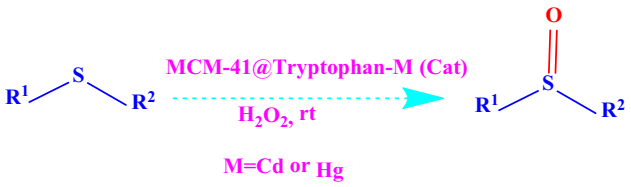
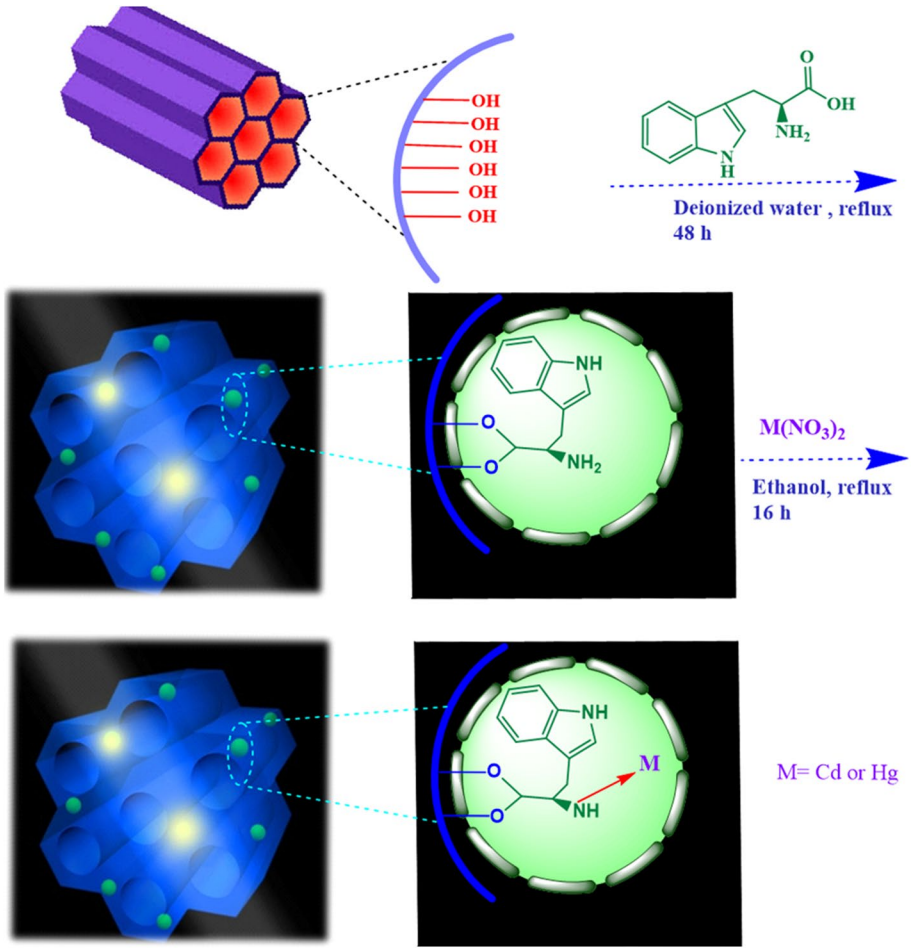
1 Introduction

Catalysis plays a main role on new approaches to the development of green chemistry principles [1]. Homogeneous catalysts are recommended for performing a wide range of chemical transformations considering their performance in activity and selectivity. However their separation and recovery after a reaction is a challenge. Immobilizing homogeneous catalysts on supports was introduced to overcome their separation and reuse problems. This immobilization affords catalyst with the advantages of both homogeneous (selectivity, tunability, and homogeneous sites) and heterogeneous (separation, recovery, and reuse) catalysts [2–4]. During the recent years, immobilization of homogeneous catalysts on various solid supports has been of huge interest [5–7]. Even though, immobilization of homogeneous catalysts usually reduces the catalytic activity [8, 9]. Nanotechnology, a fast-growing area, can overcome this drawback and act as efficient bridges between homogeneous and heterogeneous catalysts [10]. Among various nanoparticles, mesoporous materials cover large number of applications in heterogeneous support for the immobilization of homogeneous catalysts [11–14]. mesoporous silica MCM-41 became the most attractive member of the family M41S due to its unique properties like high surface area, good thermal stability, low mass density and large pore volume [15–17] and it has been a focus for many potential applications as nanoscience [18], catalysis [19, 20], environmental purification [21] and drug delivery [22]. MCM-41 consists of an array of uniform hexagonal channels of tunable size [21, 23]. Because of the nature of MCM-41 pore structure, it has the availability of a large number of free silanol groups [20]. Attachment of active molecules to the inner pore surfaces can be exploited as catalyst for different types of

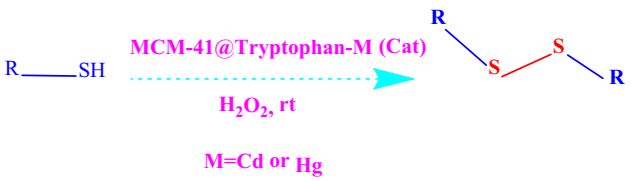


Scheme 2 The oxidation of sulfides into sulfoxides

Scheme 1 Synthesis of MCM-41@Tryptophan-M



reactions. Loaded metal complexes into the channel walls is highly desirable in the development of reusable catalysts [24, 25]. Tryptophan is an amino acid present in all natural proteins and has an indole functional group [26]. The present study has focused on the immobilization of tryptophan on the surface of MCM-41 as a novel amino acid based solid support. The selective conversion of thiols to disulfides so that no additional oxidation takes place, is important for many chemists both from the biological (as an examples the disulfide bond plays an important role to form and stabilization of the structure of peptides and protein) and synthesis points of view (including the use of a wide variety of disulfides as volcanizing agents for rubbers and elastomers, which gives these materials extraordinary elasticity) [27–30]. Likewise, sulfoxides are beneficial synthetic intermediates in the synthesis of chemically and biologically crucial molecules such as therapeutic agents, pharmaceutical and fine chemical industries [11, 31–34]. Oxidation of sulfides and thiols is the usual route for preparation of corresponding sulfoxides and disulfides. Although this reaction has been studied extensively [35–40], it is necessary to introduce procedures that are more simple, mild, efficient and especially selective without over oxidation to the corresponding materials. Herein we report MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg as new, highly efficient, reusable and highly stable catalysts for oxidative coupling of thiols into disulfides and oxidation of sulfides to sulfoxides under mild condition with controlled oxidation.



Scheme 3 The oxidative coupling of thiols into disulfides

2 Experimental

2.1 Materials and Instrumentation

Chemicals and solvents used in this work were purchased from Merck and Sigma-Aldrich and were used without further purification. X-ray diffraction (XRD) patterns were recorded on a MPD diffractometer of X'pert with Cu–Kα radiation under the conditions of 40 kV and 40 mA. SEM images were recorded using FESEM-TESCAN MIRA3. Fourier transforms infrared (FTIR) spectra of KBr disks were measured on a VERTEX70 model BRUKER FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 instrument. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to obtain the metal content of the nanocatalyst. The elemental analysis of the samples was done by Energy-dispersive X-ray spectroscopy (EDAX, TSCAN).

2.2 Preparation of MCM-41

Synthesis of MCM-41mesoporous silica was carried out by following a similar methodology according to the literature method [41] using cetyltrimethylammonium bromide (CTAB) as the structure directing agent, tetraethylorthosilicate (TEOS) as Si source and sodium hydroxide as pH controlling agent. A typical synthesis gel was prepared by

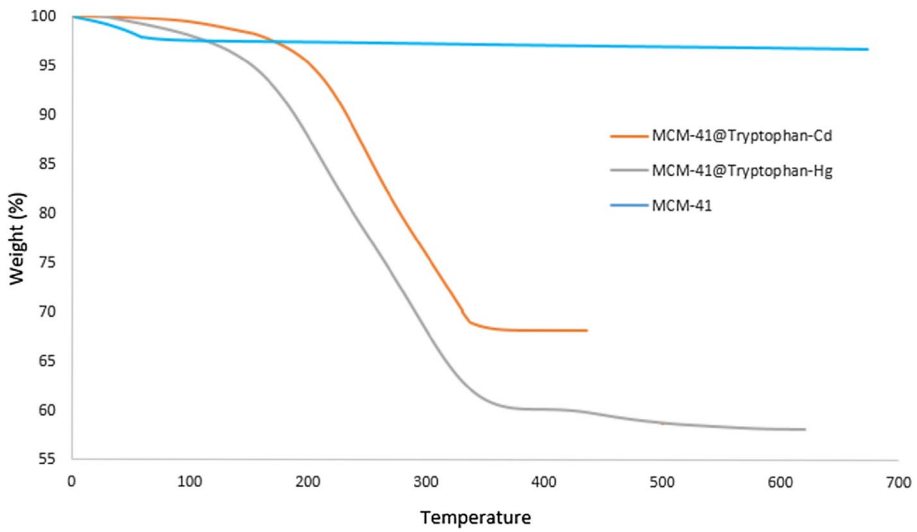


Fig. 1 TGA curves of MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg

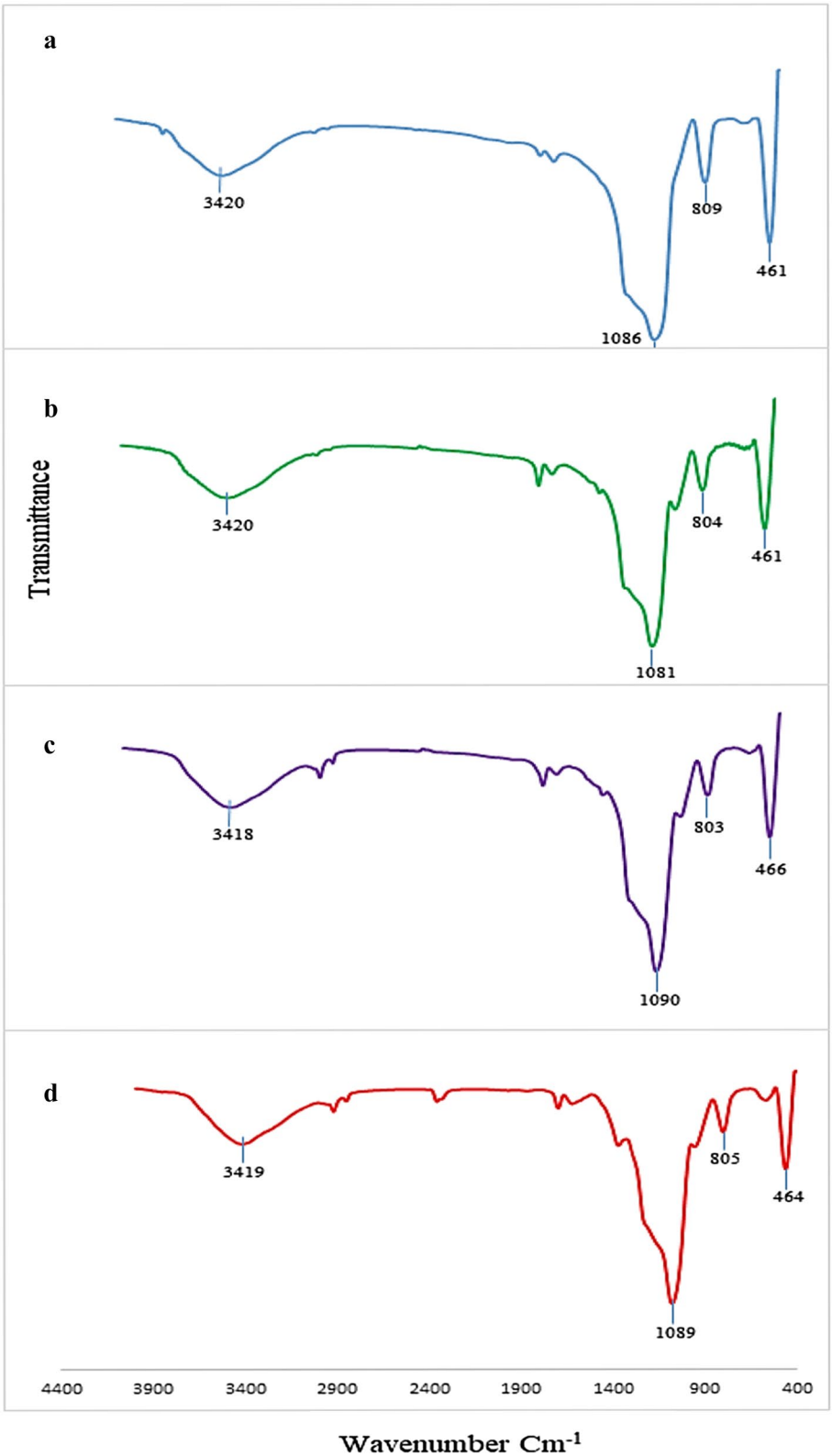


Fig. 2 FT-IR spectra of **a** MCM-41, **b** MCM-41@ Tryptophan, **c** MCM-41@ Tryptophan-Cd and **d** MCM-41 @Tryptophan-Cd

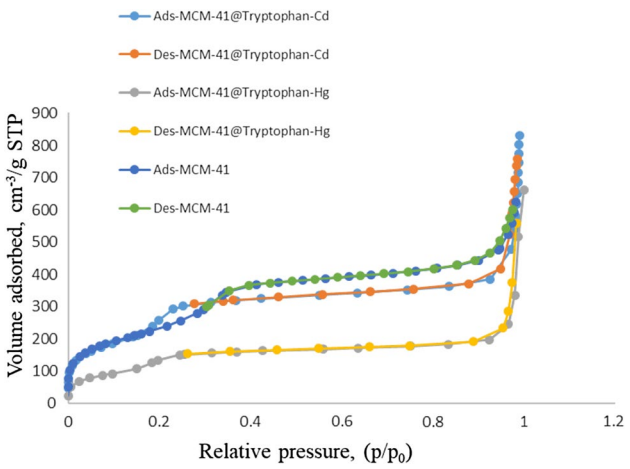


Fig. 3 Nitrogen adsorption–desorption isotherms of MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg

Table 1 Texture parameters obtained from nitrogen adsorption studies

Volume sample	S_{BET} (m^2/g)	Pore diameter by BJH method (nm)	Pore (cm^3/g)
MCM-41	987.5	3.6	1.2852
MCM-41@Tryptophan-Cd	294.1	2.1	0.4369
MCM-41@Tryptophan-Hg	141.2	1.8	0.3732

adding surfactant CTAB (1 g) to a solution of deionized water (480 mL) and NaOH (2 M, 3.5 mL) which was stirred at 80 °C. When the solution became uniform, 5 ml of TEOS was slowly added into the solution. The resulting solution was stirred for 2 h at the ambient temperature. The resulting product was filtered, washed with distilled water and dried at 60 °C. Finally the collected product was calcined at 550 °C for 5 h with rate of 2 °C/min to remove the surfactant. This mesoporous material is designated as MCM-41.

2.3 Preparation of MCM-41@Tryptophan-M (Cd and Hg)

Grafting of the ligand (Tryptophan) to MCM-41 was performed by stirring of MCM-41(1 g) with tryptophan (1.5 g) in deionized water (50 mL) at 50 °C for 48 h under reflux condition. The resulting white solid was filtered, washed with deionized water and dried at 50 °C. Finally MCM-4@Tryptophan-Cd or Hg was prepared by stirring the above mentioned solid (1 g) with $Cd(NO_3)_2{\cdot}4H_2O$ or $Hg(NO_3)_2$ (2.5 mmol), in ethanol under reflux condition for 16 h. Eventually, the resulting solid was filtered, washed with ethanol and dried at 50 °C (Scheme 1).

2.4 General Procedure for the Oxidation of Sulfides to Sulfoxide

A mixture of sulfide (1 mmol), H_2O_2 (0.5 mL) and MCM-41@Tryptophan-M (Cd or Hg) (0.005 g) was stirred under

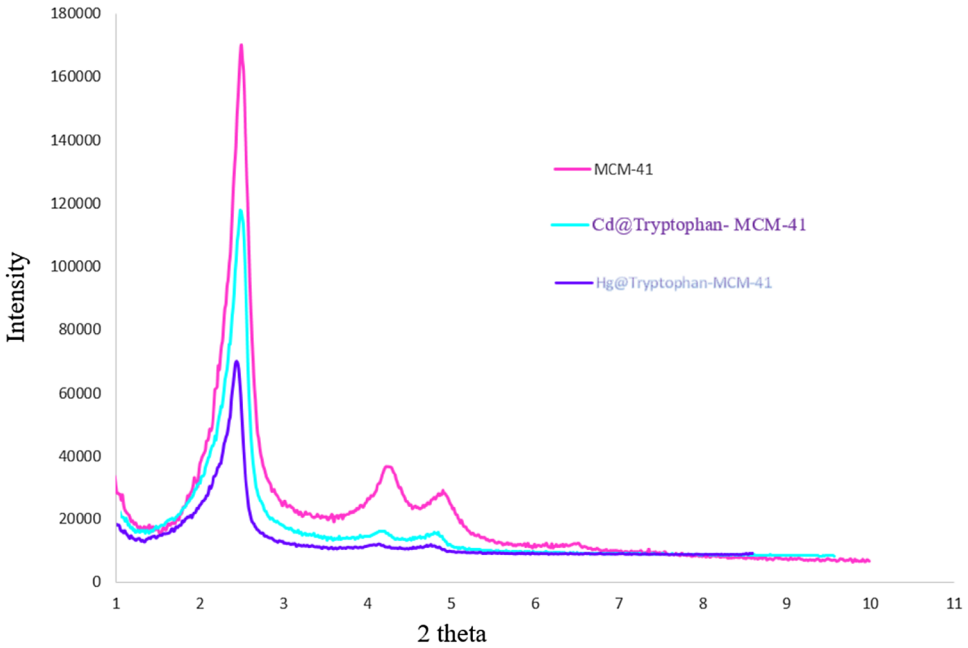


Fig. 4 XRD patterns of the MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg

neat conditions at room temperature for appropriate time and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and washed with ethyl acetate. Finally, ethyl acetate was evaporated, and then pure product with excellent yield was obtained by crystallization from ethanol (Scheme 2).

2.5 General Procedure for the Oxidation of Thiols to Disulfides

General experimental procedure for the oxidative coupling of thiols is as following: MCM-41@Tryptophan-M (Cd or Hg) (0.005) was added to a mixture of thiol (1 mmol) and H_2O_2 (0.5 mL) in ethanol (3 mL). Then the mixture was magnetically stirred for the appropriate time at room temperature. The progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration and the mixture was washed with ethyl acetate. The product was extracted with ethyl acetate. After the evaporation of ethyl acetate, the pure product was obtained by crystallization from ethanol (Scheme 3).

3 Results and Discussion

3.1 Catalyst Synthesis and Characterization

Here-in, we report the synthesis and characterization of MCM-41@Tryptophan-M (Cd and Hg) for the first time. Also we studied their applications as novel heterogeneous and recoverable catalysts in the synthesis of sulfoxides and disulfides from sulfides and thiols respectively. Both

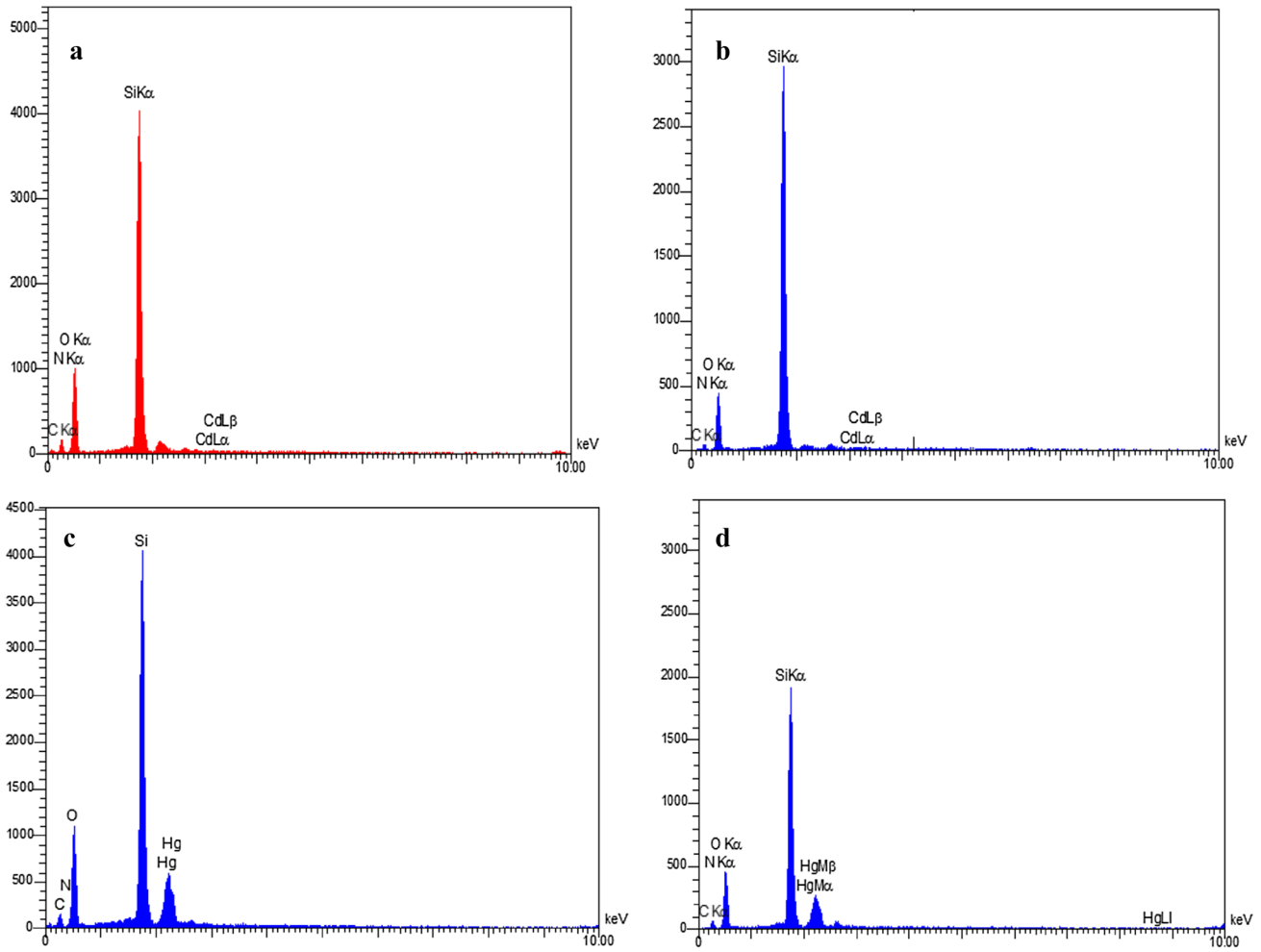


Fig. 5 EDS pattern of **a** MCM-41@Tryptophan-Cd, **b** recovered MCM-41@Tryptophan-Cd, **c** MCM-41@Tryptophan-Hg and **d** recovered MCM-41@Tryptophan-Hg

processes were carried out at room temperature. The MCM-41@Tryptophan-M were prepared using reaction of the immobilized tryptophan on MCM-41 with Cd or $Hg(NO_3)_2$. Tryptophan complexes supported on nanoporous MCM-41 have been characterized by a variety of techniques.

The TGA curves of the MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg indicates the weight loss of the organic material as they decompose upon heating (Fig. 1). The weight loss (< 200) in the samples attributed to removal of physically and chemically adsorbed surface hydroxyl groups and organic solvents [42]. The 32% mass loss for MCM-41@Tryptophan-Cd and 42% for MCM-41@Tryptophan-Hg between 200 and 500 °C are assigned to the thermal decomposition of tryptophan ligands grafting to the MCM-41. Based on these results, the well grafting Cd-tryptophan and Hg-tryptophan into MCM-41 channels is verified.

Figure 2 shows FT-IR spectra for MCM-41, MCM-41@Tryptophan, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg. Curve a, in Fig. 2, is FT-IR spectrum for the MCM-41. It shows three peaks at 809 and 1086 cm^{-1} corresponding to the symmetric and asymmetric Si–O–Si

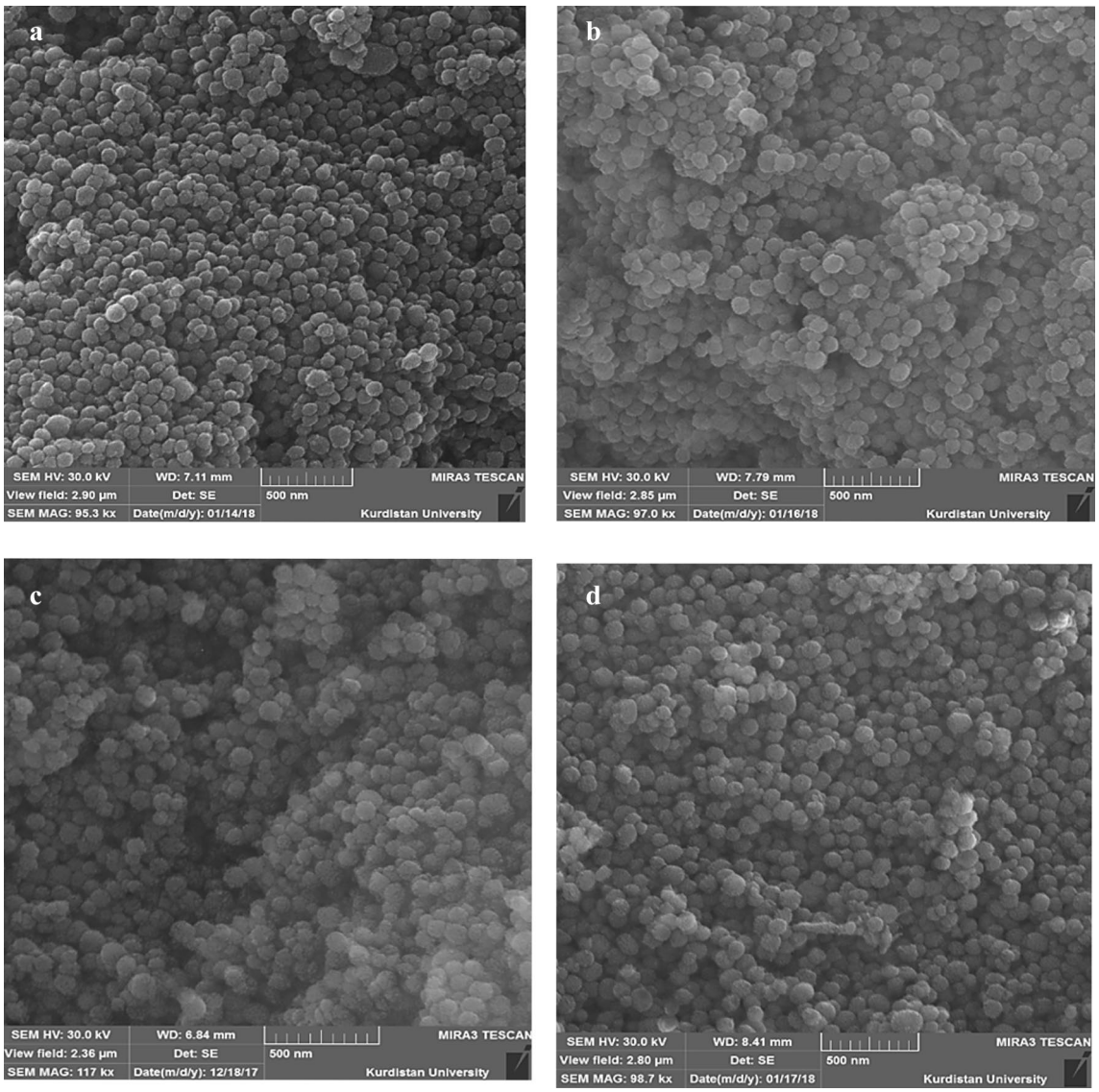


Fig. 6 SEM images of **a** MCM-41@Tryptophan-Cd, **b** recovered MCM-41@Tryptophan-Cd, **c** MCM-41@Tryptophan-Hg and **d** recovered MCM-41@Tryptophan-Hg

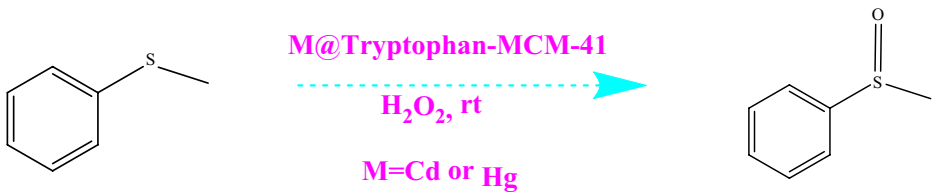
vibration respectively and at 461 cm^{-1} due to the Si–O bending vibration. For the silanol (O–H), which are attached to the MCM-41 framework, stretching vibration bands appeared at 3420 cm^{-1}. In the spectrum of the MCM-41@Tryptophan, the presence of anchored tryptophan to the solid surface was confirmed by aliphatic C–H stretching vibrations appeared at about 2926 cm^{-1} and C–N stretching vibration at 1630 cm^{-1}. The FT-IR spectrum of Cd and Hg onto MCM-41@Tryptophan show bands at 1090 and 1089 cm^{-1} corresponding to the asymmetric Si–O–Si vibration, 803 and 805 cm^{-1} attributed to the symmetric Si–O–Si vibration, 466 and 464 cm^{-1} assignable to the Si–O bending vibration. These phenomena indicate that the MCM-41 structure remained unchanged after immobilization of metals complexes on the MCM-41. The band near 1385 cm^{-1} of the MCM-41@Tryptophan is attributed to $\nu(NH_2)$ bending; this band is shifted to lower wavenumber in the spectrum of the MCM-41@Tryptophan-Cd and MCM-41 @Tryptophan-Hg due to the coordination of the amino group nitrogen atom to the metal ion [4].

The N_2 adsorption–desorption isotherms results of MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg are shown in Fig. 3. As shown, the BET surface area decreased with the anchored of tryptophan complex on the MCM-41 sample, which are in agreement with the XRD result. The Barret–Joyner–Halenda average pore diameter (D_{BJH}), the Brunauer–Emmett–Teller surface area (S_{BET}) and the Total pore volumes (V_{total}) of the samples are summarized in Table 1. Reduction of Physical parameters of nitrogen isotherms was observed with functionalization of the mesoporous material. These results confirm that metals tryptophan complexes were bonded on the MCM-41.

The low-angle XRD patterns of MCM-41, MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg are shown in Fig. 4. The XRD pattern of MCM-41 shows a typical three-peak pattern with very strong reflection at $2\theta = 2.51°$ for d100 and two other weaker reflections at $2\theta = 4.30°$ and 4.91° for d110 and d200, respectively, that can be indexed to well-ordered one-dimensional hexagonal mesoporous structure of mesoporous MCM-41 [43]. Upon post grafting of M-tryptophan into MCM-41, decreased intensity of the (100) diffraction peak and the disappearance of the (110) and (100) peaks are observed, indicating that the mesostructure ordering was decreased due to successful dispersion of Cd and Hg complexs into the pore channels of MCM-41 [25]. Also, the position of d100 reflection in the samples was retained and the patterns were similar, which means that the MCM-41 structure remained unchanged after the functionalization steps.

The metal content of MCM-41@Tryptophan-M was determined using EDS. The EDS patterns of MCM-41@Tryptophan-M and recovered MCM-41@Tryptophan-M

Table 2 Optimization of the reaction conditions for the oxidation of methylphenyl sulfide as model compound



Entry	Solvent	MCM-41@Tryptophan-M (mg)		H_2O_2 (mL)	Time (min)		Yield (%)[a]	
		Cd	Hg		Cd	Hg	Cd	Hg
1	Solvent free	3	3	0.5	35	30	91	94
2	Solvent free	5	5	0.5	35	30	94	95
3	Solvent free	7	7	0.5	30	35	95	95
4	Solvent free	5	5	0.4	50	45	90	93
5	ETOH	5	5	0.5	120	110	87	87
6	Ethyl acetate	5	5	0.5	150	145	80	85
7	Acetonitrile	5	5	0.5	200	190	75	85

[a]Isolated yields

Table 3 Oxidation of sulfides into sulfoxides in the presence of MCM-41@Tryptophan-M (mg) at room temperature

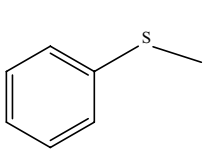
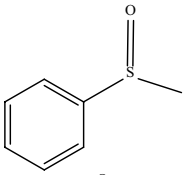
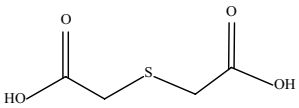
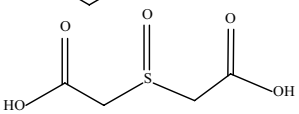
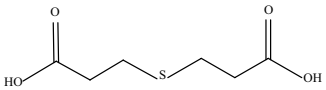
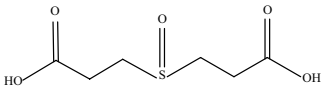
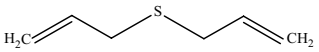
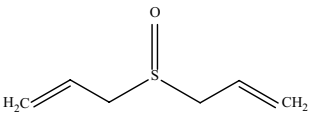
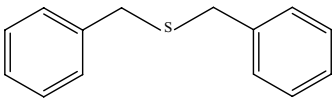
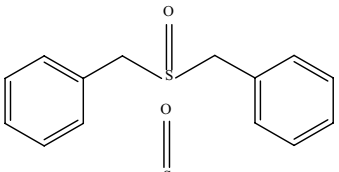
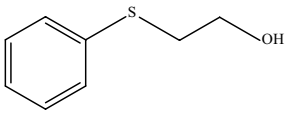
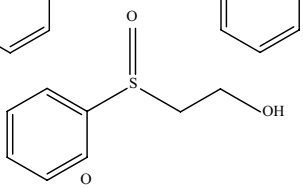
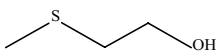
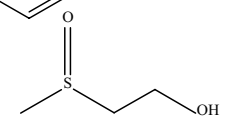
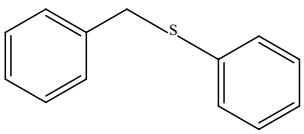
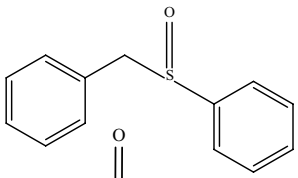
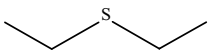
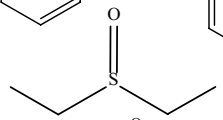
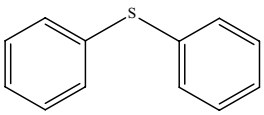
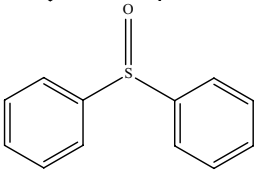
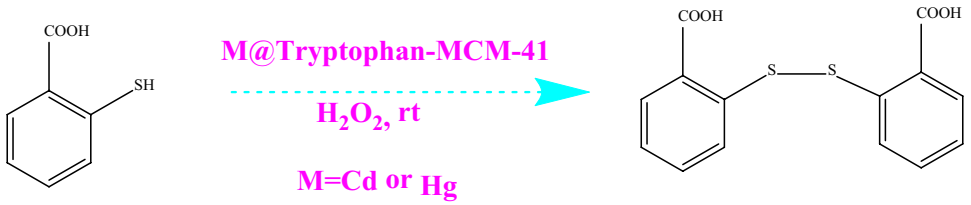
Entry	Sulfide	Product	Time (min)		Yield %	
			Cd	Hg	Cd	Hg
1			35	30	94	95
2			2	2	99	99
3			3	2	98	99
4			2	1	90	93
5			7	6	91	94
6			2	2	95	95
7			2	1	93	94
8			5	5	91	91
9			5	3	93	95
10			10	7	89	91

Table 4 Optimization of the reaction conditions for the oxidation of 2-mercaptobenzoic acid as model compound



Entry	Solvent	MCM-41@Tryptophan-M (mg)		H_2O_2 (mL)	Time (min)		Yield (%)[a]	
		Cd	Hg		Cd	Hg	Cd	Hg
1	ETOH	3	3	0.5	25	15	91	91
2	ETOH	5	5	0.5	5	5	96	96
3	ETOH	7	7	0.5	10	5	96	97
4	ETOH	5	5	0.4	7	7	91	91
5	Solvent free	5	5	0.5	25	10	76	86
6	Ethyl acetate	5	5	0.5	40	85	86	83
7	Acetonitrile	5	5	0.5	100	190	88	84

[a]Isolated yields

catalysts are shown in Fig. 5. As shown in Fig. 5a, b EDS spectrum of MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Cd in the eighth recovery, shows the presence of O, Si, C, N and Cd species in the catalyst. Also Fig. 5c, d shows the presence of O, Si, C, N and Hg species in the MCM-41@Tryptophan-Hg and MCM-41@Tryptophan-Hg in the eighth recovery. To investigate the amount of Cd and Hg in unreacted MCM-41@Tryptophan-M ICP-OES (inductively coupled plasma optical emission spectrometry) analysis was performed and they found to be 0.20 and 0.85 mmol g^{-1} respectively.

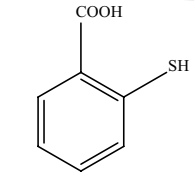
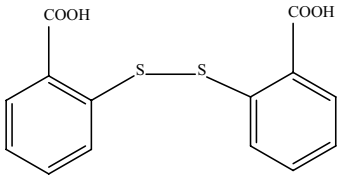
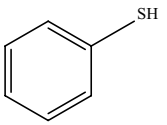
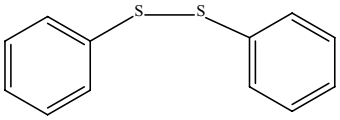
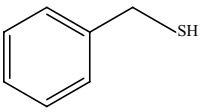
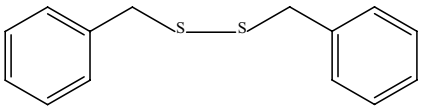
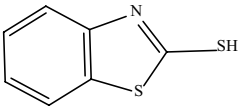
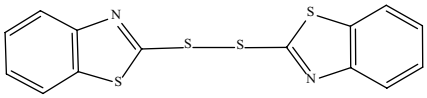
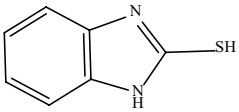
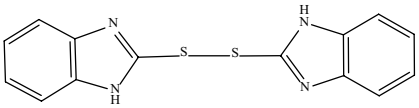
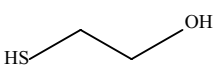
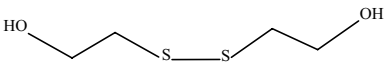
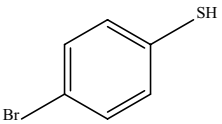
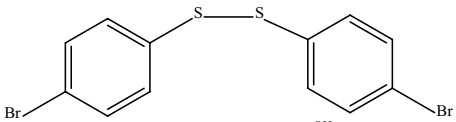
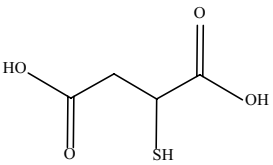
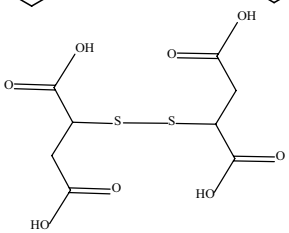
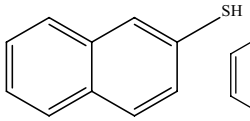
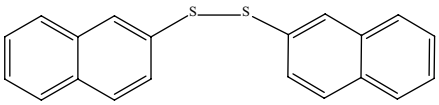
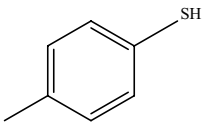
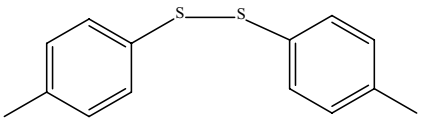
The morphological of the catalysts was investigated using SEM technique. Figure 6 shows the SEM photographs of MCM-41@Tryptophan-M catalysts and recovered MCM-41@Tryptophan-M catalysts. As shown in this figure, the nanoparticles are made up of uniform nanosized spherical particles. Also no significant changes in the surface morphology occurred after recovery.

3.2 Catalytic Studies

As the first part of our program, the catalytic activity of MCM-41@Tryptophan-M (Cd and Hg) was examined for the oxidation of sulfides into corresponding sulfoxides (Scheme 2). To optimize reaction conditions, we evaluated the influence of different solvents, amount of catalysts and amount of H_2O_2 on oxidation of methyl phenyl sulfide as a model reaction (Table 1). Initially, the influence of different solvents, and then the effect of catalysts amount, and subsequently, effect of amount of H_2O_2 on the oxidation of methyl phenyl sulfide were investigated. As shown in Table 1, the best results were obtained with 0.005 g of catalysts in solvent free condition and 0.5 ml H_2O_2 at room temperature for two catalysts. (Table 2, entry 2). After the optimization of the reaction condition several sulfides with different functional groups in optimal conditions, have been converted to their corresponding sulfoxides (Table 3).

In second part of our study, we evaluated the catalytic activity of MCM-41@Tryptophan-M (Cd and Hg) in oxidative coupling thiols into their corresponding disulfides (Scheme 3). In order to optimize reaction conditions, 2-mercaptobenzoic acid was chosen as a model and the influence of different amounts of catalyst, H_2O_2, and the nature of solvent were studied (Table 4). Table 4 indicates that 0.005 g of catalysts and 0.5 ml H_2O_2 in ethanol were the best conditions for oxidative coupling of thiols to disulfides at room temperature in both catalysts. (Table 4, entry 2). Then we investigated oxidative coupling of various thiols with

Table 5 Oxidative coupling of thiols into disulfides in the presence of MCM-41@Tryptophan-M (mg) at room temperature

Entry	Sulfide	Product	Time (min)		Yield %	
			Cd	Hg	Cd	Hg
1			5	5	96	96
2			1	1	95	95
3			2	1	91	92
4			4	4	91	91
5			10	10	94	94
6			10	5	90	94
7			25	15	89	91
8			2	2	98	98
9			1	1	90	90
10			2	1	93	95

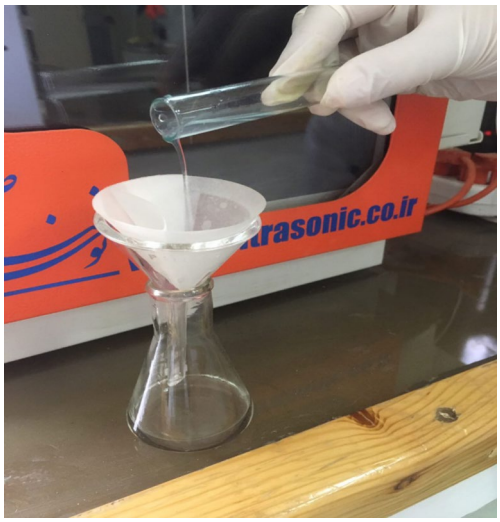


Fig. 7 Recovery of MCM-41@Tryptophan-M by simple filteration

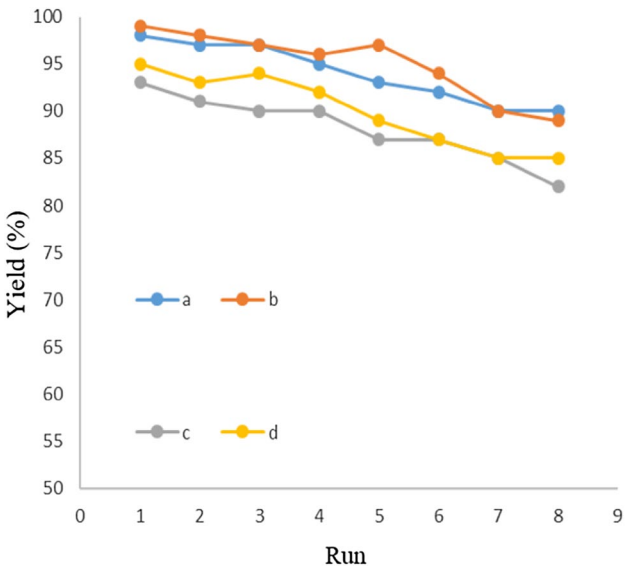


Fig. 8 Reusability of MCM-41@Tryptophan-M (*a*) Cd and (*b*) Hg catalysts for oxidation of 3,3′-thiodipropionic acid and (*c*) Cd and (*d*) Hg oxidative coupling of 4-methylthio ethanol

optimal conditions (Table 5). As shown in Tables 3 and 5, thiols and sulfide were successfully converted to the corresponding material, and all products were obtained in high to excellent yields in the short reaction time. There is no over oxidation to sulfone (for oxidation of sulfides) or sulfoxide (for the oxidative coupling of thiols) was observed; so the present heterogeneous systems could be applicable for the chemo selective oxidative coupling of thiols and oxidation of sulfides.

3.3 Reusability of the Catalyst

Finally, the reusability of the MCM-41@Tryptophan-Cd and MCM-41@Tryptophan-Hg were evaluated for the oxidation of 3,3′-thiodipropionic acid and oxidative coupling of 4-methylthio ethanol as a model reaction under the optimized conditions. Upon completion of the reaction, the catalyst was recovered using simple filtration from the reaction mixture after each cycle and washed with the ethyl acetate, and subjected to the next run (Fig. 7).

As shown in Fig. 8, the catalysts could be reused up to eight cycles without detectable lose of catalytic activity. The recovered catalysts were characterized by SEM (Fig. 5b, d). They indicate that the morphology of the recovered MCM-41@Tryptophan-M (Cd and Hg) catalysts and unreacted catalysts are similar. During the catalyst recycling, the decreased activity ascribed to the low leaching of Cd and Hg from MCM-41 functionalized.

3.4 Comparison of the Catalyst

To demonstrate the merit of MCM-41@Tryptophan-M (Cd and Hg) the catalytic data was compared with that found in the literature, the results for the oxidation of dibenzyl sulfide and benzyl mercaptan as representative examples. As shown in Table 6 MCM-41@Tryptophan-M (Cd and Hg) show a better catalytic activity in terms of the best reaction time and high yield.

4 Conclusion

We successfully immobilized Tryptophan-Cd and Tryptophan-Hg onto functionalized mesoporous MCM-41. The MCM-41@Tryptophan-M catalysts were characterized by FT-IR, XRD, TGA, BET, SEM, EDX and ICP-OES techniques. These catalysts catalyzed oxidation of sulfides to sulfoxides and thiols to disulfides in the presence of H_2O_2. The main findings of this work are simple work-up, short reaction times, and high yields of products. The catalysts are selective and they can easily separated using a simple filtration without any loss of their catalytic activity.

Table 6 Comparison results of prepared catalysts for the oxidation of dibenzyl sulfide and benzyl mercaptan with previously reported procedure

Entry	Substrate	Reagent	Time (min)	Yield (%)	Ref.
1	Dibenzyl sulfide	MCM-41	60	20	This work
2	Dibenzyl sulfide	MCM-41@Tryptophan	60	10	This work
3	Dibenzyl sulfide	MCM-41@Tryptophan-Cd	7	91	This work
4	Dibenzyl sulfide	MCM-41@Tryptophan-Hg	6	94	This work
5	Dibenzyl sulfide	Zr(IV)/isatin-MCM-48	30	99	[44]
6	Dibenzyl sulfide	Ni-salen-MCM-41	145	97	[11]
7	Dibenzyl sulfide	Cd-salen-MCM-41	137	96	[11]
8	Dibenzyl sulfide	Fe_3O_4/salen of Cu(II)	120	97	[40]
9	Dibenzyl sulfide	Fe_3O_4@SiO_2@DOPisatin-Ni	20	96	[35]
10	Dibenzyl sulfide	Fe_3O_4@SiO_2@DOPisatin-Cu	15	96	[35]
11	Benzyl mercaptan	MCM-41	60	23	This work
12	Benzyl mercaptan	MCM-41@Tryptophan	60	13	This work
13	Benzyl mercaptan	MCM-41@Tryptophan-Cd	2	91	This work
14	Benzyl mercaptan	MCM-41@Tryptophan-Hg	1	92	This work
11	Benzyl mercaptan	VO@MCM-41-Cys	60	98	[41]
12	Benzyl mercaptan	Ni-SMTU@boehmite	225	95	[39]
13	Benzyl mercaptan	Fe_3O_4-Adenine-Zn	90	96	[45]
14	Benzyl mercaptan	M-salen-MNPs (M: Cr, Zn, Cd, Co, Ni)	60	99	[28]
15	Benzyl mercaptan	DSA@MNPs	60	90	[46]
16	Benzyl mercaptan	Cu-Schiff base@MCM-41	60	91	[27]

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