Revised: 2 February 2018

FULL PAPER

Synthesis of new zirconium complex supported on MCM-41 and its application as an efficient catalyst for synthesis of sulfides and the oxidation of sulfur containing compounds

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INTRODUCTION 1

During the recent increasing interest in the field of organocatalysis, heterogeneous catalysts are attracted attention over homogeneous catalysts because of their simplicity in recovery and regeneration.^[1-3] Various approaches have been suggested for the immobilization of homogeneous transition metal complexes on silica, zeolites, alumina and other metal oxides. Despite their easy synthesis, anchoring of homogeneous transition metal catalysts on solid supports often decreases the catalytic activity or efficiency.^[4–7] Therefore in the last few years, nano-catalysts have been used as ideal heterogeneous supports because they can act as efficient bridge between homogeneous and heterogeneous catalysts.^[8-11] Silica mesoporous molecular sieves have specific advantages, including ease of preparation, low cost, excellent

thermal and chemical stability, large internal surface area

In the present work, we report synthesis of new zirconium complex supported on mesoporous silica by anchoring of adenine on the wall of functionalized MCM-41, then reacted with ZrOCl₂. The resultant MCM-41-Adenine-Zr was characterized by FT-IR, XRD, TEM, SEM, TGA, EDX, ICP and BET techniques. It was exhibited that the MCM-41-Adenine-Zr can be used as an efficient and thermally stable nanocatalyst for the oxidation of sulfides, oxidative coupling of thiols and synthesis of sulfides. Moreover, this heterogeneous catalyst can be easily recovered from the reaction mixture by simple filtration and reused for several consecutive cycles without noticeable change in its catalytic activity.

KEYWORDS

disulfide, recoverability, sulfide, sulfoxide, zirconium

and high concentration of surface Si-OH groups.[12-16] MCM-41 is member of mesoporous molecular sieves with hierarchical structure and hexagonally packed arrays that can be used as catalyst supports.^[17] These nanoparticles, because of their high surface area and good catalytic activity and high efficiency, have a wide range of applications in the removal of chromate and arsenate, drug delivery systems, extraction, adsorption, catalysis support and recycling of expensive homogeneous catalysts.^[18-21]

Sulfoxides, disulfides and sulfides are useful in the chemical industries and play a vital role in some medicines and biological processes. During the recent increasing interest in synthesis of these compounds, varieties of catalysts have been received considerable attention. However, the drawback of catalysts is their separation from the reaction mixture using tedious procedure. This problem can be overcome using nanocatalysts which can be easily removed with simple and inexpensive procedure such as filtration.^[22-25] 2 of 12

On the other hand, heterogeneous zirconium oxide catalysts have been developed to promote the oxidation reaction under relatively mild conditions. In spite of tremendous effort dedicated to the development of heterogeneous zirconium oxide complexes, up to date, there are no report researches about the synthesis of sulfides in the presence above mentioned complex.^[26–28]

In the present study, as a part of our continuing interest in the development of efficient and new heterogeneous catalysts for organic synthesis, we present our results on the preparation and characterization of novel MCM-41-Adenine-Zr nanoparticles, and its catalytic application for the oxidation of sulfides, oxidative coupling of thiols and synthesis of sulfides via reaction of aryl halides with sulfur. The simple work up, excellent yield, use of easy to handle procedure, short reaction time, inexpensive and non-toxic catalyst; makes this protocol both attractive and economically viable for above mentioned reactions. More importantly, up to date, there are no reported for synthesis of sulfides in presence zirconium catalyst.

2 | EXPERIMENTAL

2.1 | Materials and physical measurements

All solvents and materials used in this work are purchased from Merck, Fluka and Sigma-Aldrich and used without further purification. TGA measurement of the nanostructures was carried out on Shimadzu DTG-60 instrument with a temperature range from 80 to 700 °C. The amount of metal was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The surface morphology of nanostructures was investigated with measuring SEM using FESEM-TESCAN MIRA3. The elemental analysis of the samples was taken by Energy-dispersive X-ray spectroscopy (EDAX, TSCAN). Transmission electron microscopy (TEM) analysis was obtained with a Philips CM10 microscope operating at 200 Kv. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 80 v model using the KBr pellets in the range of 400–4000 cm⁻¹. Melting points of products were determined with an Electrothermal 9100 apparatus. Powder X-ray diffraction (XRD) measurements were taken using Co radiation source with a wavel ength l = 1.78897 Å, 40 kV.

2.2 | Preparation of mesoporous silicaanchored MCM-41-Adenine-Zr

Mesoporous MCM-41 was synthesized through the sol-gel method by mixing 1 g of cetyltrimethylammonium bromide (CTAB), as structure directing template agent, to a solution containing 3.5 ml of NaOH solution (2 M) and deionized water (480 ml) and stirred at 80 °C, then 5 ml of tetraethylorthosilicate (TEOS) as the silica source was gradually added to the solution and the mixture stirred at the same temperature for 2 h. Finally, the resulting mixture was filtered and washed with deionized water and dried in an oven at 60 °C followed by calcination at 823 K for 5 h at a rate of 2 °C/min to remove the residual surfactants. The collected product affords pure silica MCM-41. Functionalization of MCM-41 was performed by adding 1 g of MCM-41 to a solution of 3chloropropyltrimethoxysilane (1.5 ml) in 25 ml of toluene (30 ml). The reaction mixture was stirred under reflux conditions and allowed to stand for 24 h. The white precipitate was collected (MCM-41-Cl) and washed with nhexane and dried under vacuum. Then, adenine (0.27 g)was added to a suspension of the MCM-41-Cl (1 g) in toluene (30 ml). The resulting mixture stirred under reflux conditions for 48 h, filtered, washed thoroughly with ethanol/water and dried in vacuum. For the synthesis of MCM-41-Adenine-Zr catalyst, MCM-41-Adenine and $ZrO_2Cl.8H_2O(0.8 g)$ were mixed in ethanol (30 ml). Then the mixture was refluxed for 16 h, filtered, washed thoroughly with ethanol and dried in vacuum (Scheme 1).



SCHEME 1 Synthesis of MCM-41-Adenine-Zr

2.3 | General procedure for the preparation of sulfoxides

In this step, MCM-41-Adenine-Zr catalyst (4 mg) was added to mixture of sulfide (1 mmol) and H_2O_2 (0.4 ml) and stirred at room temperature under solvent-free condition for appropriate time. Upon completion of the reaction progress as monitored by TLC, the catalyst was filtered and washed with ethyl acetate. Finally, ethyl acetate was removed to give the pure sulfoxides and the products were obtained in good to high yields.

2.4 | General Procedure for the oxidative coupling of thiols

In summary, a mixture of thiol (1 mmol), H_2O_2 (0.4 ml) and MCM-41-Adenine-Zr (3 mg) was stirred at room temperature under solvent-free condition. Completion of the reaction and the compound purity were monitored by TLC. After the reaction was completed, the separation of catalyst from reaction products was performed by the filtration process and the catalyst washed with ethyl acetate. Finally, the solvent of product was removed to give the pure disulfides.

2.5 | General procedure for the sulfides synthesis

A mixture of sulfur (1 mmol), aryl halide (1 mmol), KOH (0.7 g) and MCM-41-Adenine-Zr catalyst (0.05 g) in DMSO (2 ml) was stirred at 130 °C. Then the progress of reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated by filtration and the reaction mixture was extracted with ethyl acetate. The organic extract was washed twice with water and dried with anhydrous Na_2SO_4 . Finally, the solvent was evaporated to give corresponding sulfide.

2.6 | Selected spectral data

2.6.1 | Dodecyl methyl sulfoxide: (Table 2, entry 7)

¹H NMR (400 MHz, DMSO, ppm): $δ_{\rm H}$ = 0.87 (t, *J*=6.6, 3H), 1.26–1.71 (m, 20H), 2.95(s, 3H), 3.09 (t, *J*=8, 2H).

2.6.2 | Methyl phenyl sulfoxide (Table 2, entry 8)

¹H NMR (400 MHz, CDCl₃, ppm): $\delta_{\rm H}$ = 2.75 (s, 3H), 7.52–7.62 (m, 2H), 7.66–7.69 (m, 3H).

2.6.3 | 1,2-Di-p-tolyldisulfane (Table 4, entry 2)

¹H NMR (400 MHz, CDCl₃, ppm): δ_{H} = 2.36 (s, 6H), 2.41 (s, 3H), 7.11-7.59 (m, 8H).

2.6.4 | 2,20-Dimethoxy diphenyl sulfide (Table 6, entry 1)

¹H NMR (400 MHz, DMSO, ppm): δ_{H} = 6.96–7.36 (m, 8H), 3.82 (s, 6H).

2.6.5 | Diphenyl sulfide (Table 6, entry 2)

¹H NMR (400 MHz, DMSO, ppm): δ_{H} = 6.30–7.34 (m, 6H), 7.37–7.46 (m, 4H).

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

In continuation of our previous efforts on the application of supported metal catalyst on mesoporous silica in organic reactions,^[12,29–31] herein, we report for the first time the synthesis and characterization an environmentally friendly and novel MCM-41-Adenine-Zr catalyst (Scheme 1), and investigated its application as an efficient heterogeneous and recoverable catalyst in the synthesis of sulfoxides (Scheme 2), disulfides (Scheme 3) and sulfides (Scheme 4).

A plausible reaction mechanism for the synthesis MCM-41-Adenine-Zr is shown in Scheme 2.

3.2 | Catalyst characterization

The resultant MCM-41-Adenine has been characterized by XRD, FT-IR, TEM, SEM, TGA, EDS, ICP and BET techniques.



SCHEME 2 MCM-41-Adenine-Zr catalyzed the oxidation of sulfides to sulfoxides



SCHEME 3 MCM-41-Adenine-Zr catalyzed the oxidation of sulfides to sulfoxides



SCHEME 4 Proposed mechanism for oxidation of sulfides in presence of MCM-41-Adenine-Zr as catalyst

The crystalline structures of the MCM-41 (blue curve) and MCM-41-Adenine-Zr (red curve) catalyst were determined by powder X-ray diffraction (XRD). As seen in Figure 1, the XRD pattern of MCM-41 shows the presence of a single intense peak and two weak peaks assigned to (1 0 0), (1 1 0) and (2 0 0) reflections at $2\theta = 2.38$, 3.81 and 4.69°, respectively. These spectra reflect hexagonal mesoporous structure of MCM-41. Also, an overall decrease in diffraction (100) at $2\theta = 2.26^{\circ}$ upon post anchoring of zirconium complex on the wall of functionalized MCM-41 was noticed which is due to the difference in the scattering contrast of the pores and the walls of nanochannels of MCM-41. More importantly, The XRD pattern of the MCM-41-Adenine-Zr catalyst and MCM-41 were indicated which the texture of initial material of the MCM-41upon post anchoring of zirconium complex on MCM-41 was retained.



FIGURE 1 The XRD patterns of MCM-41 (blue curve) and MCM-41-Adenine-Zr (red curve)

The morphology of the MCM-41 and MCM-41-Adenine-Zr were obtained using scanning electron microscopy (SEM) technique. SEM images of the MCM-41 and MCM-41-Adenine-Zr are given in Figure 2. As shown in this Figure, MCM-41 and MCM-41-Zr was made up of quite homogeneous and uniform spherical particles and no significant changes in the morphology occurred



FIGURE 2 SEM images of a) calcined MCM-41and b) MCM-41-Adenine-Zr catalyst

upon the insertion of zirconium complex group onto MCM-41.

The energy-dispersive X-ray spectroscopy (EDX) analysis is shown in Figure 3. In order to determine the kinds of elements in MCM-41-Adenine-Zr, the EDS analysis of MCM-41-Adenine-Zr was performed; which EDS patterns of this catalyst shows the presence of peaks associated with Si, O, N, C and Zr species in the catalyst. Also, in order to determine the exact amount of Zr loaded on modified MCM-41 nanoparticles, ICP-OES analysis was performed and it was found to be 0.29 mmol g^{-1} .

As shown in Figure 4, the size of MCM-41-Adenine-Zr catalyst was determined with transmission electron microscopy (TEM). TEM analysis of the synthesized MCM-41-Adenine-Zr shows that particles have highly ordered long-range hexagonal arrangement. It should be mentioned that the size of the MCM-41-Adenine-Zr catalyst is around 125 nm.

Blue curve in Figure 5 is the spectrum of MCM-41, red curve is the spectrum of MCM-41-Cl, violet curve is the spectrum of MCM-41-Adenine and green curve is the spectrum of MCM-41-Adenine-Zr. FT-IR spectrum of MCM-41 (blue spectrum) shows a bending vibration at 463 cm⁻¹. Furthermore, absorption peaks appearing at around 1100–1200 cm^{-1} and 3000–3600 cm^{-1} are due to Si-O-Si asymmetric stretching and the silanol OH groups, respectively. In FT-IR spectra of MCM-41-Cl (red spectrum), the presence of the anchored (3-choloropropyl) trimethoxysilane is identified by C-H stretching vibrations that appear at 2955 and 2851 cm⁻¹. In the FT-IR spectra of MCM-41-Adenine (violet spectrum), stretching vibrations of C=C and C=N has been identified by adsorption bands at 1311-1436 and 1609-1692 cm⁻¹. FT-IR spectrum of MCM-41 (green spectrum) obtained after adsorption of Zr on to MCM-41-Adenine.

Thermo-gravimetric analysis (TGA) of the organic groups supported on the surface of bare MCM-41 is



FIGURE 3 EDX spectrum of MCM-41-Adenine-Zr







FIGURE 4 TEM images of MCM-41-Adenine-Zr catalyst at different magnifications



FIGURE 5 FT-IR spectrum for bare MCM-41 (blue spectrum), MCM-41-Cl (red spectrum), MCM-41-Adenine (violet spectrum) and MCM-41-Adenine-Zr (green spectrum)

presented in Figure 6. In all samples, the first step of weight loss below 200 °C corresponds to the removal of the physically and chemically adsorbed solvents or surface hydroxyl groups, and the other weight loss in the range of 200-500 °C is related to the decomposition of the organic layers on the surface of MCM-41. TGA curve of the MCM-41-Adenine-Zr (blue curve) shows a weight loss more than 29% from 200 to 500 °C, resulting from the decomposition of immobilized organic spaces on the MCM-41 surface. On the basis of this result, the well grafting of organic groups including Zr complex on the MCM-41 is verified.

As shown in Figure 7, the N₂-adsorption and desorption isotherms results are measured in order to determine the textural properties. MCM-41-Adenine-Zr was degassed at 100 °C under an argon gas flow for 3 h prior to the measurements. These results are shown in Table 1 indicating the functionalized MCM-41 have smaller BET surface area, narrower pore diameter and lower absorption volume. The results of N₂ adsorption and desorption isotherms of MCM-41 and MCM-41-Adenine-Zr are



FIGURE 6 TGA curves of MCM-41 (red curve) and MCM-41-Adenine-Zr (blue curve)



FIGURE 7 Nitrogen adsorption/desorption isotherms of MCM-41 and MCM-41-Adenine-Zr

TABLE 1 Texture parameters obtained from nitrogen adsorption studies

Sample	SBET (m ² g ⁻¹)	Pore diameter by BJH method (nm)	Pore volume (cm ³ g ⁻¹)
MCM-41	1113.7	2.39	1.39
MCM-41-Adenine-Zr	313.90	1.12	0.446

attributed to the anchoring of zirconium complex on the inner surface of the pores.^[28]

As shown in Figure 8, the X-ray mapping of MCM-41-Adenine-Zr was investigated in order to evaluate the dispersion of Zr active sites in the catalyst. It was found that the elemental map images were indicated the good dispersion of Zr on surface of catalyst.

3.3 | Catalytic studies

In the first part of our program, the catalytic activity of MCM-41-Adenine-Zr catalyst was examined in oxidation of sulfides to sulfoxides using H_2O_2 (30%) as oxidant at room temperature (Scheme 3). In order to find the best reaction conditions, dipropyl sulfoxide was prepared as a model compound in the presence of different amounts of MCM-41-Adenine-Zr catalyst using H₂O₂ (30%) in various solvents as well as solvent-free conditions (Table 2). These reactions were tested in ethanol, acetonitrile and ethyl acetate and solvent-free condition. After optimizing the solvent, catalyst amounts were varied from 0.003 to 0.007 g for reactions carried out at room temperature. It was found that there is a general trend of increasing conversion of sulfide to sulfoxide with increasing amount of catalyst. As shown in Table 2, 0.004 g MCM-41-Adenine-Zr and 0.4 ml H₂O₂ under solvent-free condition at room temperature was found to be ideal reaction conditions for the conversion of dipropylsulfide to the dipropylsulfoxide.



FIGURE 8 The X-ray map analysis of MCM-41-Adenine-Zr catalyst

TABLE 2	Optimization of oxidation of sulfides to the corresponding sulfoxides using MCM-41-Adenine-Zr nanoparticles under various
conditions	

Entry	Solvent	H ₂ O ₂	Catalyst (mg)	Time (min)	Yield (%) ^a
1	Acetonitrile	0.4	4	105	85
2	Ethanol	0.4	4	120	92
3	Ethyl acetate	0.4	4	85	79
4	Solvent-Free	0.4	3	70	79
5	Solvent-Free	0.4	4	55	97
6	Solvent-Free	0.5	4	50	96
7	Solvent-Free	0.4	5	50	98
8	Solvent-Free	0.4	7	45	98

^aIsolated yields.

The generality of this approach has been demonstrated by facile oxidation of a wide range of sulfides with different functional groups to their corresponding products in the presence of MCM-41-Adenine-Zr catalyst as summarized in Table 3. All products are obtained in the short reaction time and in good to excellent yields.

A plausible reaction mechanism for oxidation of sulfides is shown in Scheme 4.^[35]

As the second part of our organic study, we turned our attention towards the synthesis of disulfide compounds in high efficiency in the presence of MCM-41-Adenine-Zr as catalyst and H₂O₂ as the oxidant at room temperature under solvent-free conditions (Scheme 5).

In order to optimize the reaction conditions, we started our investigation under the influence of varying the amount of MCM-41-Adenine-Zr catalyst and different amount of H2O2 for the oxidative coupling of 4methylbenzenethiol as a model substrate using various solvents such as acetonitrile, ethanol, ethyl acetate as well as solvent-free conditions (Table 4).

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Entry	Substrate	Product	Time (min)	Yield (%) ^b	M.p.(°C)	
					Found	Reported
1	Dipropylsulfide	2a	55	96	Oil	Oil ^[32]
2	Diethylsulfide	2b	45	95	Oil	Oil ^[32]
3	Dibenzylsulfide	2c	35	97	132	127-129 ^[32]
4	Benzylphenylsulfide	2d	40	90	122	117-119 ^[33]
5	Tetrahydrothiophene	2e	5	92	Oil	Oil ^[13]
6	Dimethylsulfide	2f	60	91	Oil	Oil ^[34]
7	Dodecylmethylsulfide	2 g	50	97	63-65	61-65 ^[34]
8	Methylphenylsulfide	2 h	55	97	30-32	33-34 ^[33]
9	2-(Phenylthio)ethanol	2i	65	89	Oil	Oil ^[34]

^aReaction conditions: MCM-41-Adenine-Zr (0.004 g), sulfide (1 mmol), H₂O₂ (0.4 mL), solvent-Free condition at room temperature. ^bIsolated yields.

 $\frac{R^{3}-SH}{3a-h} \xrightarrow{MCM-41-Adenine-Zr}_{Solvent.Free, H_{2}O_{2}, rt} \frac{R^{3}}{S^{-S_{R}}} R^{3}$

SCHEME 5 MCM-41-Adenine-Zr catalysed the oxidative coupling of thiols into disulfides

It is noteworthy that, systematic studies are carried out in the presence of different amounts of the catalyst to investigate the effect of the catalyst. We have found that a higher yield was observed when the amount of the catalyst was increased.

TABLE 4	Optimization of	oxidative coupling	of thioles using	MCM-41-Adenine-Zr	nanoparticles und	ler various conditions
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Entry	Solvent	H_2O_2	Catalyst (mg)	Time (min)	Yield (%) ^a
1	Acetonitrile	0.4	3	180	91
2	Ethanol	0.4	3	115	94
3	Ethyl acetate	0.4	3	165	94
4	Solvent-Free	0.4	2	85	83
5	Solvent-Free	0.4	3	65	96
6	Solvent-Free	0.4	4	60	95
7	Solvent-Free	0.4	5	55	96
8	Solvent-Free	0.5	3	60	95

^aIsolated yields.

TABLE 5 Oxidative coupling of thiols into disulfides using H_2O_2 in the presence of MCM-41-Adenine-Zr^a

			Time	Yield	M.p. (°C)	
Entry	Substrate	Product	(min)	(%) ^b	Found Rej	ported
1	Phenylmethanethiol	4a	45	96	68-71	69-70 ^[36]
2	4-Methylbenzenethiol	4b	65	96	35-38	36-38 ^[32]
3	Naphthalene-2-thiol	4c	30	97	137	134-136 ^[32]
4	2-Mercaptobenzoic acid	4d	40	89	275	278-284 ^[32]
5	Benzo[d]thiazole-2-thiol	4e	15	94	90-93	174–176 ^[32]
6	2-Mercaptoethanol	4f	30	98	Oil	Oil ^[32]
7	4-Bromothiophenol	4 g	55	89	89-92	86-90 ^[32]
8	Benzo[d]oxazole-2-thiol	4 h	60	93	90-92	94–96 ^[36]

^aReaction conditions: MCM-41-Adenine-Zr (0.003 g), thiol (1 mmol), H₂O₂ (0.4 ml), solvent-Free condition at room temperature. ^bIsolated yields.



SCHEME 6 Proposed mechanism for oxidative coupling of thiols in presence of MCM-41-Adenine-Zr as catalyst



SCHEME 7 MCM-41-Adenine-Zr catalyzed the synthesis of sulfides

MCM-41-Adenine-Zr catalyst (0.003 g) in the presence of H_2O_2 (0.4 ml) under solvent-free conditions at room temperature was found to be ideal reaction conditions for the oxidative coupling of 4-methylbenzenethiol. In order to gain further insight into this process and with optimal conditions in hand, oxidation reactions for a wide range of thiols with different functional groups were performed in the presence of MCM-41-Adenine-Zr as catalyst under mild and completely heterogeneous conditions at room temperature (Table 5). After reaction completion, the products were extracted by simple filtration and prepared in the short reaction time and in good to excellent yields.

The proposed mechanism for this process using H_2O_2 as oxidant in the presence MCM-41-Adenine-Zr catalyst is outlined in Scheme 6.^[35]

We finally investigated the synthesis of sulfide derivatives in moderate to excellent yields.

In this work, sulfur was selected for the direct synthesis of organic sulfides from aryl halides using MCM-41-Adenine-Zr as catalyst (Scheme 7). In order to find the best reaction conditions, the reaction of iodobenzene and sulfur in the presence of MCM-41-Adenine-Zr catalyst was selected as a model reaction and influence of solvent, temperature and amount of catalyst and the type of base on the outcome of reaction has been investigated (Table 6).

The reaction of sulfur (1 mmol), iodobenzene (1 mmol) and KOH (0.7 g) was optimized in presence of different amount of catalyst using various solvents such as EtOH, DMSO, DMF, CH₃CN and PEG. Among various solvents screened (Table 1, entries 1–8), it is found that the reaction was highly effected in polar aprotic solvents such as DMSO and dimethylformamide (DMF).

TABLE 6 Optimization of the reaction conditions for the C-S coupling using MCM-41-Adenine-Zr catalyst

Entry	Solvent	Base	Temp. (°C)	Catalyst (mg)	Time (min)	Yield (%) ^a
1	DMF	КОН	130	50	240	11
2	PEG	КОН	130	50	240	N.R
3	CH ₃ CN	КОН	130	50	240	N.R
4	EtOH	КОН	130	50	240	N.R
5	H_2O	КОН	130	50	240	N.R
6	Toluene	КОН	130	50	240	N.R
7	DMSO	КОН	80	50	240	10
8	DMSO	КОН	100	50	240	15
9	DMSO	КОН	130	50	240	66
10	DMSO	КОН	130	30	240	23
11	DMSO	КОН	130	70	240	68
12	DMSO	КОН	130	100	240	69
13	DMSO	NaOH	130	50	240	N.R
14	DMSO	Na ₂ CO ₃	130	50	240	N.R
15	DMSO	Et ₃ N	130	50	240	21

^aIsolated yields.

TABLE 7 Synthesis of symmetrical sulfides via reaction of sulfur and aryl halides using DMSO in the presence of MCM-41-Adenine-Zr^a

			Time	Yield	M.p. (°C)	
Entry	Substrate	Product	(min)	(%) ^b	Found Reported	l
1	2-Methoxyiodobenzene	6a	210	61	Oil	Oil ^[22]
2	Iodobenzene	6b	240	66	Oil	Oil ^[37]
3	4-Bromonitrobenzene	6c	80	52	158-161	159–161 ^[38]
4	Bromobenzene	6d	360	65	Oil	Oil ^[37]
5	Benzylbromide	6e	180	59	44-46	43 ^[39]
6	4-Iodotoluene	6f	560	50	Oil	Oil ^[38]
7	4-Chloronitrobenzene	6 g	120	41	160-162	159–161 ^[38]
8	4-Bromotoluene	6 h	620	33	Oil	Oil ^[38]
9	Chlorobenzene	6i	660	28	Oil	Oil ^[37]
10	4-Iodonitrobenzene	6ј	60	50	157-160	159–161 ^[38]

^aReaction conditions: MCM-41-Adenine-Zr (0.05 g), sulfur (1 mmol), aryl halide (1 mmol) and KOH (0.7 g), DMSO (2 ml) at 130 °C. ^bIsolated yields.





FIGURE 9 Reusability of MCM-41-Adenine-Zr in the oxidati on of dipropyl sulfide (red column), the oxidative coupling of 4-methylbenzenethiol (green column) and the synthesis of diphenylsulfide (blue column)

SCHEME 8 Proposed mechanism for synthesis of sulfides in the presence of MCM-41-Adenine-Zr

In order to optimize the catalyst amount, various quantities of catalyst were used in synthesis of sulfides. Therefore, we studied the outcome of the reaction with various amounts of catalyst. It can be seen that an increase in the quantity of catalyst from 0.03 to 0.05 g enhances the product yield from 23 to 66%. It should be mentioned that a greater amount of catalyst has substantially less effect on the yield and time of the reaction (Table 6, entry 11, 12).

As shown in Table 6, we observed that the best results were obtained in presence 0.05 g MCM-41-Adenine-Zr catalyst, 0.7 g KOH in DMSO (2 ml) at 130 °C.

With optimal conditions in hand, in order to explore the generality and scope of this protocol, a variety of aromatic halides were employed to the synthesis of TABLE 8 Comparison of MCM-41-Adenine-Zr for the oxidation of methylphenylsulfide with previously reported procedure

Entry	Substrate	Catalyst	Time (min)	Yield (%) ^a
1	Methylphenylsulfide	Cd-salen-MCM-41	150	98 ^[25]
2	Methylphenylsulfide	TsOH	240	88 ^[41]
3	Methylphenylsulfide	SiO ₂ -W ₂ -Im	150	91.9 ^[42]
4	Methylphenylsulfide	VO-2A3HP-MCM-41	120	96 ^[13]
5	Methylphenylsulfide	Ni-SMTU@boehmite	75	97 ^[43]
6	Methylphenylsulfide	NBS	270	93 ^[44]
7	Methylphenylsulfide	Zr-oxide@MCM-41	300	98 ^[26]
8	Methylphenylsulfide	MCM-41-Adenine-Zr	55	97 [this work]

^aIsolated yields.

sulfides derivatives in the presence of MCM-41-Adenine-Zr for the appropriate time in moderate to excellent yields.

The results of this study are summarized in Table 7.

After successful synthesis of sulfides derivatives, a plausible reaction mechanism for the synthesis of this product is proposed in Scheme 8.^[40]

3.4 | Recyclability of the catalyst

In order to investigate the recyclability of the catalyst, synthesis of sulfides via reaction of iodobenzene with sulfur, methylphenylsulfide oxidation of to the methylphenylsulfoxide and oxidative coupling of 4methylbenzenethiol to the corresponding disulfide were examined. The catalyst was separated by filtration and dried after each run, recycled and reused without considerable decrease of its catalytic activity. Figure 9 shows the yield of 3 times of synthesis of sulfides and 6 times for the oxidation of sulfides and oxidative coupling of thiols. This observation can simply describe that the leaching of zirconium from MCM-41-Adenine-Zr is very negligible for these reactions. According to ICP-OES analysis, the exact amount of Zr loaded on modified mesostructured for the conversion of dipropyl sulfide to the dipropyl sulfoxide at least for six consecutive cycles was found to be 0.21 mmol/g. Decrease in the catalyst efficiency and lengthening of the reaction time.

3.5 | Catalyst leaching Study

The amounts of zirconium leaching in synthesis of diphenyl sulfide was studied by checking the Zr loading amount before and after recycling of the catalyst by ICP-OEIS technique. It was found that the amount of zirconium in fresh catalyst and the recycled catalyst after 3 times recycling is 0.29 and 0.19 mmolg⁻¹, respectively. Therefore, ICP-OEIS analysis indicated that zirconium leaching of this catalyst is very low.

3.6 | Comparison of the catalyst

The efficiency of this nanocatalyst is demonstrated by comparing our results on the synthesis of methylphenylsulfoxde with the previous methods in the literatures (Table 8). As it can be seen in Table 8, easy catalyst/product separation and catalyst recycling, high yield, easy preparation of the catalyst using cheap and commercially available materials, short reaction time, use of non-toxic ligand, and stability are several benefits of this protocol.

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4 | CONCLUSION

In summary, preparation of new zirconium complex supported onto surface of mesoporous silica as a reusable, green and highly efficient catalyst have been performed. The structure of new catalyst was characterized by FT-IR, TGA, EDS, TEM, ICP-OES, XRD, BET and SEM. MCM-41-Adenine-Zr was separable from the reaction mixture by filtration, reused for consecutive several cycles and used for the oxidation of sulfides, oxidative coupling of thiols and synthesis of sulfides in a short time under mild conditions in moderate to high yields.

ACKNOWLEDGEMENTS

The authors are deeply grateful to Erfan Ghadermazi, University of Kurdistan and University of Ilam for financial support of this research project.

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REFERENCES

- [1] J. Davarpanah, A. R. Kiasat, RSC Adv. 2015, 5, 7986.
- [2] T. Tamoradi, A. Ghorbani–Choghamarani, M. Ghadermazi, New J. Chem. 2017, 41, 11714.
- [3] B. Karimi, M. Rafiee, S. Alizadeh, H. Vali, *Green Chem.* 2015, 17, 991.
- [4] S. Sahoo, A. Bordoloi, S. B. Halligudi, *Catal Surv Asia*. 2011, 15, 200.
- [5] R. V. Chaudhari, Platinum Metals Rev. 2011, 55, 180.
- [6] K. Leus, Y. Y. Liu, P. V. D. Voort, Catal. Rev. 2014, 56, 1.
- [7] L. Jankovic, D. Gournis, K. Dimos, M. A. Karakassides, T. Bakas, J. Phys: Conf Ser 2005, 10, 178.
- [8] S. Shylesh, V. Schünemann, W. R. Thiel, Angew. Chem. Int. Ed. 2010, 49, 3428.
- [9] M. Hajjami, B. Tahmasbi, RSC Adv. 2015, 5, 59194.
- [10] J. Davarpanah, A. R. Kiasat, Catal. Commun. 2013, 42, 98.
- [11] C. W. Lim, I. S. Lee, Nano Today 2010, 5, 412.
- [12] F. Havasi, A. Ghorbani-Choghamarani, F. Nikpour, Micro. Meso. Mat. 2016, 224, 26.
- [13] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Khanmoradi, Appl. Organometal. Chem. 2016, 30, 705.
- [14] W. Y. Hao, J. C. Sha, S. R. Sheng, M. Z. Cai, *Catal. Commun.* 2008, 10, 257.
- [15] M. Cai, H. Zhao, Y. Huang, J. Mol. Catal. A. 2005, 238, 41.
- [16] J. Davarpanah, A. R. Kiasat, RSC Adv. 2014, 4, 4403.
- [17] A. J. Chen, X. R. Chen, C. Y. Mou, J. Chin. Chem. Soc. 2010, 57, 820.
- [18] A. Corma, H. Garcia, Adv. Synth. Catal. 2006, 348, 1391.
- [19] R. Tian, H. Zhang, M. Ye, X. Jiang, L. Hu, X. Li, X. Bao, H. Zou, Angew. Chem. Int. Ed. 2007, 46, 962.
- [20] H. Yoshitake, T. Yokoi, T. Tatsumi, Chem. Mater. 2002, 14, 4603.
- [21] M. Vallet-Regi, F. Balas, D. Arcos, Angew. Chem. Int. Ed. 2007, 46, 7548.
- [22] A. Ghorbani-Choghamarani, Z. Taherinia, RSC Adv. 2016, 6, 59410.
- [23] H. Weissbacha, F. Etiennea, T. Hoshib, S. H. Heinemannc, W. T. Lowtherd, B. Matthewsd, G. S. Johne, C. Nathane, N. Brote, *Arch. Biochem. Biophys.* 2002, 397, 172.
- [24] A. R. Hajipour, M. Mostafavi, A. E. Ruoho1, Sulfur. Silicon. Relat. Elem. 2009, 184, 1920.
- [25] M. Darabi, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Transition Met. Chem.* 2017, 42, 703.

- [26] M. Hajjami, L. Shiri, A. Jahanbakhshi, Appl. Organometal. Chem. 2015, 29, 668.
- [27] T. Zhang, Y. Q. Deng, W. F. Zhou, C. T. Au, S. F. Yin, *Chem. Eng. J.* 2014, 240, 509.
- [28] M. Hajjami, Z. Yousofvand, Catal. Lett. 2015, 145, 1733.
- [29] M. Nikoorazm, A. Ghorbani-Choghamarani, H. Mahdavi, S. M. Esmaeili, *Micro. Meso. Mater.* 2015, 211, 174.
- [30] N. Noori, M. Nikoorazm, A. Ghorbani-Choghamarani, *Micro. Meso. Mater.* 2016, 234, 166.
- [31] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, Appl. Organomet. Chem. 2015, 29, 328.
- [32] A. Ghorbani-Choghamarani, Z. Darvishnejad, M. Norouzi, Appl. Organometal. Chem. 2015, 29, 170.
- [33] A. Jabbari, H. Mahdavi, M. Nikoorazm, A. Ghorbani-Choghamarani, J. Porous Mater. 2015, 22, 1111.
- [34] J. Zeyer, P. Eicher, S. G. Wakeham, R. P. Schwarzenbach, Appl. Environ. Microbiol. 1987, 53, 2026.
- [35] T. Tamoradi, B. Mehraban-Esfandiari, M. Ghadermazi, A. Ghorbani–Choghamarani, *Res. Chem. Intermed.* 2018, 44, 1363.
- [36] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, *Catal. Communic.* 2015, 60, 70.
- [37] P. Zhao, H. Yin, H. Gao, C. Xi, J. Org. Chem. 2013, 78, 5001.
- [38] Y. Zhou, J. Chem. Res. 2016, 40, 305.
- [39] B. H. Mackl, R. G. Mayrick, Trans. Faraday Soc. 1962, 58, 238.
- [40] A. Rostami, A. Rostami, N. Iranpoor, M. A. Zolfigo, Tetrahedron Lett. 2016, 57, 192.
- [41] B. Yu, C. X. Guo, C. L. Zhong, Z. F. Diao, L. N. He, *Tetrahedron Lett.* 2015, 55, 1818.
- [42] S. Thurow, V. A. Pereira, D. M. Martinez, D. Alves, G. Perin, R. G. Jacob, E. J. Lenard[~]ao, *Tetrahedron Lett.* **2011**, *52*, 640.
- [43] A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, *RSC Adv.* 2016, *6*, 56458.
- [44] B. Karimi, D. Zareyee, J. Iran, Chem. Soc. 2008, 5, Sl03.

How to cite this article: Tamoradi T, Ghorbani-Choghamarani A, Ghadermazi M. Synthesis of new zirconium complex supported on MCM-41 and its application as an efficient catalyst for synthesis of sulfides and the oxidation of sulfur containing compounds. *Appl Organometal Chem.* 2018;e4340. https://doi.org/10.1002/aoc.4340