Full paper

Applied
Organometallic
Chemistry

Received: 22 March 2015 Revised: 10 May 2015 Accepted: 4 June 2015

(wileyonlinelibrary.com) DOI 10.1002/aoc.3348

Zirconium oxide complex-functionalized MCM-41 nanostructure: an efficient and reusable mesoporous catalyst for oxidation of sulfides and oxidative coupling of thiols using hydrogen peroxide

Maryam Hajjami*, Lotfi Shiri and Azar Jahanbakhshi

Zirconium oxide complex-functionalized mesoporous MCM-41 (Zr-oxide@MCM-41) as an efficient and reusable catalyst is reported for the oxidation of sulfides into sulfoxides using hydrogen peroxide (H_2O_2) as the oxidant, with short reaction times in good to excellent yields at room temperature under solvent-free conditions. Also, a simple and efficient method is reported for the oxidative coupling of thiols into corresponding disulfides in good to high yields using H_2O_2 as oxidant in the presence of Zr-oxide@MCM-41 as recoverable catalyst in ethanol at room temperature. A series of sulfides and thiols possessing functional groups was successfully converted into corresponding products. After completion of reactions the catalyst was easily separated with simple filtration from the reaction mixture and reused for several consecutive runs without significant loss of catalytic efficiency. The mesoporous catalyst was characterized using Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller surface area measurements, X-ray diffraction, transmission and scanning electron microscopies, energy-dispersive X-ray spectroscopy and thermogravimetric analysis. Copyright © 2015 John Wiley & Sons, Ltd.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: Zr-oxide@MCM-41; hydrogen peroxide; oxidation; sulfoxides; disulfides

Introduction

Catalytic processes play a fundamental role in chemical and pharmaceutical industries.[1,2] While very selective and active homogeneous catalysts have been developed, it is often difficult to isolate the products and to recover the catalyst for reuse.[3] This difficulty can be overcome using heterogeneous catalysts, which in general allow a simple separation of products and catalyst.[4] Therefore, the preparation and engineering of nanostructured porous silicate materials have been greatly explored as heterogeneous catalysts owing to their characteristics of high surface area and uniform mesoporous nano-order.[5,6] Particularly, the MCM-41 molecular sieve has allowed development of catalysts applicable in many industrial processes.[5–12] Features such as a hexagonal packed array of unidirectional mesopores (between 2 and 10 nm) with narrow pore size distribution, highly ordered structure, high thermal stability, high surface area (up to 900 $m^2\ g^{-1}$) and high specific pore volume (up to 1.3 $ml\ g^{-1}$) are mainly responsible for its high adsorption capacity even of bulky molecules.[8] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channels.[9] Therefore, some transition metal complexes on functionalized MCM-41 support have been prepared and successfully used in organic reactions.[10] In this light, some zirconium oxide complexes on functionalized MCM-41 support can be prepared and successfully used in organic reactions. Meanwhile, the catalytic properties of these materials rely on the presence of active sites in their frameworks. In fact, numerous studies have been performed aiming to modify pure siliceous MCM-41 in order to increase its applicability.[11,12] Also, the potential advantage of these materials (simplified recovery and reusability) as compared with homogeneous systems can lead to environmentally benign chemical processes. In spite of tremendous effort dedicated to the immobilization of homogeneous zirconium oxide complexes over the last two decades,[13] very few examples of oxidative coupling or oxidation reactions catalysed by heterogeneous zirconium oxide catalysts have been reported.[14] So, the development of a stable heterogeneous zirconium oxide catalyst that allows for highly efficient oxidation of a wide range of sulfides and oxidative coupling of many thiols is worthwhile.

Coupling reactions such as oxidative coupling of thiols into corresponding disulfides and also oxidation of organic functional groups such as oxidation of sulfides into sulfoxides are useful transformations for the synthesis of new molecules, as well as for various medical, biological, materials and nanotechnological applications.[15–17] In particular, sulfoxides are valuable synthetic intermediates for the production of a range of chemically and biologically active

---

* *Correspondence to: Maryam Hajjami, Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran. E-mail: mhajjami@yahoo.com; m.hajjami@ilam.ac.ir*

Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

molecules including therapeutic agents such as anti-ulcer, antifungal, antibacterial, anti-atherosclerotic, antihypertensive and anti-atherosclerotic drugs as well as psychotropic and vasodilator drugs.[18,19] Omeprazole and the pesticide fipronil are two typical examples of the extensive application of these intermediates in the pharmaceutical and fine chemical industries.[20,21] Likewise, disulfide bond formation is important in peptides, bioactive molecules and oil sweetening processes. Disulfides are used in sulfonylation of enolates and other anions while some disulfides have been found to be useful as vulcanizing agents for rubber and elastomers imparting to them suitable tensile strength.[22] They are also essential moieties of biologically active compounds for peptide and protein stabilization anions. Furthermore, disulfides are more stable to organic reactions such as oxidation, alkylation and acylation compared to the corresponding free thiols, so the thiol group can conveniently be protected as a disulfide.[23]

For these reasons, many methods have been developed over the years for these oxidation reactions to be carried out efficiently. For example, oxidation of sulfides and thiols has been reported in the presence of various catalysts and using a variety of oxidants (e.g. metal oxidants, organic oxidants, peroxides, halogens and air).[15–23] Concerning green oxidants, hydrogen peroxide (H_2O_2) is usually applied for the oxidation of sulfides and thiols as a cheap and environmentally friendly oxidant, because it is inexpensive and produces only water as a side product.[24] However, many of these methods have drawbacks, such as harsh acidic conditions, long reaction times, need of expensive catalyst, unsatisfactory yields and use of non-reusable catalysts. Therefore, to overcome these limitations, we decided to design a new system for the oxidation of sulfides into sulfoxides as well as for oxidative coupling of thiols into their corresponding disulfides using H_2O_2 at room temperature in the presence of zirconium oxide complex-functionalized mesoporous MCM-41 (Zr-oxide@MCM-41) as catalyst.

Experimental

Materials

Chemicals and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and used without further purification.

Preparation of Si-MCM-41

Mesoporous Si-MCM-41 was prepared according to a literature procedure.[6] Deionized water was added to 2 M NaOH and cetyltrimethylammonium bromide (CTAB) as a surfactant template and stirred vigorously at 80°C. After clarification, tetraethylorthosilicate (TEOS) was added slowly and continuously. After 2 h of stirring, a synthetic solution was obtained with molar composition TEOS/CTAB/NaOH/H_2O = 60/3.0/1.0/1. After cooling to room temperature, the resulting solid was gathered by filtration, washed with deionized water and dried at 343 K. This was followed by calcination at 823 K for 5 h at a rate of 2°C min^{-1} to remove the residual surfactant.

Preparation of catalyst

An amount of 1.0 g of 3-aminopropyltriethoxysilane (APTES) was added to a suspension of 1 g of MCM-41 in 30 ml of *n*-hexane, which was allowed to reflux for 24 h under nitrogen atmosphere. Then, the reaction mixture was cooled to room temperature, filtered and the resulting solid washed several times with *n*-hexane. The solid was dried under vacuum to afford MCM-41-NH_2. Then, for the preparation of Schiff base@MCM-41, this solid (1 g) was refluxed with 0.147 g (1 mmol) of isatin and 0.5 ml of acetic acid in ethanol for 5 h under nitrogen atmosphere. The resulting solid (Schiff base@MCM-41) was filtered, washed with ethanol and dried in vacuum. Finally, for the preparation of Zr-oxide@MCM-41, Schiff base@MCM-41 (1.0 g) was mixed with 0.1 g (1.0 mmol) of $ZrOCl_2 \cdot 8H_2O$ in 10 ml of dry CH_3CN. The mixture was stirred at room temperature for 5 h. The solid product was obtained by filtration, washed with ethanol and dried at 60°C.

General procedure for oxidation of sulfides to sulfoxides

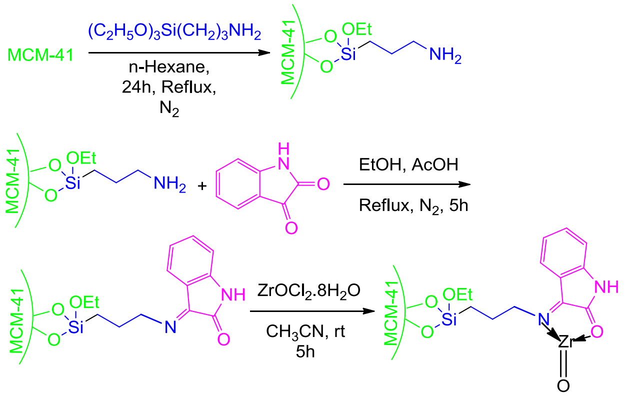
A mixture of sulfide (1 mmol), H_2O_2 (1.2 mmol) and Zr-oxide@MCM-41 (0.01 g, 1.64×10^{-4} mol%) was stirred at room temperature under solvent-free conditions, the progress of the reaction being monitored using TLC. After completion of the reaction, the catalyst was separated by simple filtration and washed with ethyl acetate. The product was then extracted with ethyl acetate (4 × 5 ml). The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Finally, the organic solvents were evaporated, affording products in good to high yields.

General procedure for oxidative coupling of thiols into disulfides

Zr-oxide@MCM-41 (0.02 g, 3.29×10^{-4} mol%) was added to a mixture of thiol (1 mmol) and H_2O_2 (1.2 mmol) in ethanol (3 ml). The mixture was then stirred for the appropriate time at room temperature. The progress was monitored using TLC. After completion of the reaction, the catalyst was separated by simple filtration and the mixture was washed with ethyl acetate (5 × 2 ml), and then the product was extracted with ethyl acetate (4 × 5 ml). The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Finally, the organic solvent was evaporated, affording products in good to high yields.

Results and discussion

In continuation of our studies concerning the introduction of new catalysts,[6] in the present work we report the preparation of Zr-oxide@MCM-41 with high catalytic activity and its application in organic reactions. The details of the supported catalyst preparation procedure are presented in Scheme 1. Mesoporous MCM-41 was synthesized using a post-grafting procedure. Furthermore, the MCM-41 surface was functionalized with commercially available APTES through siloxane linkages. Ultimately, the reaction of amino



Scheme 1. Synthesis of Zr-oxide@MCM-41.

groups with isatin led to Schiff base ligand-functionalized MCM-41 (Schiff base@MCM-41). Finally, Zr-oxide@MCM-41 was prepared using the reaction of Schiff base@MCM-41 with $ZrOCl_2{\cdot}8H_2O$. The catalyst was characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy and nitrogen adsorption–desorption isotherms.

Characterization of Zr-oxide@MCM-41

TEM and SEM images of MCM-41 and Zr-oxide@MCM-41 are shown in Figures 1 and 2. These images confirm the formation of single-phase Zr-oxide@MCM-41 nanoparticles, with spherical morphology. The average nanoparticle diameter of Zr-oxide@MCM-41 is around 40–50 nm.

In addition, the EDS spectrum of the catalyst shows the presence of zirconium species in the catalyst (Fig. S1, supporting information).

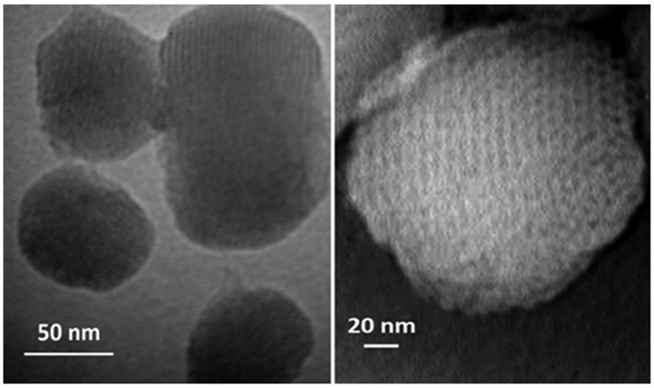


Figure 1. TEM images of MCM-41.

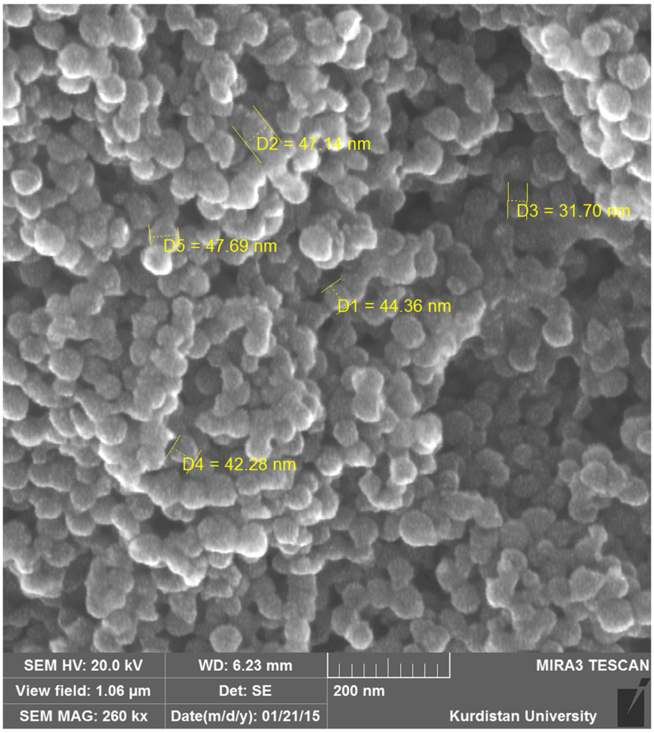


Figure 2. SEM image of Zr-oxide@MCM-41.

The EDS analysis of the catalyst indicates that the amount of C, N, O, Si, Cl and Zr is 45.08, 3.96, 28.83, 18.39, 2.61 and 1.13 mass%, respectively. These peaks suggest successful attachment of zirconium on the particle surface.

As shown in Figure 3, a series of characteristic peaks including (1 0 0), (1 1 0) and (2 0 0) reflecting the existence of mesoporous MCM-41 structure are clearly identified. Meanwhile, a broad peak at 2θ for 1 1 0 can also be clearly observed, which is assigned to amorphous Zr-oxide@MCM-41. Evidently, the samples show typical long-range order of hexagonal structure.[25]

The intensity of the (1 0 0) plane becomes weaker when metal is loaded on MCM-41, presumably resulting from the collapse of the structure of MCM-41. However, compared to the parent material, some broadening and decreased intensity of the 1 0 0 diffraction peak is observed, as well as the disappearance of the 1 1 0 and 2 0 0 peaks. The *d*-space values for these peaks are 38.85, 22.26 and 18.73 Å, respectively. A unit cell parameter (a_0) of 44.86 Å is calculated using the following equation:[26]

$$a_0 = \frac{2d \times 100}{\sqrt{3}} \tag{1}$$

Furthermore, Fig. 3 shows the XRD pattern of recovered Zr-oxide@MCM-41. The curve clearly indicates the structural stability of catalyst after being reused. The position and relative intensities of all peaks confirm this well.

One indication of bond formation between the nanoparticles and the support can be inferred from TGA. The TGA curves of MCM-41, MCM-41-NH_2, Schiff base@MCM-41, Zr-oxide@MCM-41 and reused Zr-oxide@MCM-41 show the mass loss of the organic functional group as it decomposes upon heating (Fig. S2, supporting information). TGA of Zr-oxide@MCM-41 shows three steps of weight losses and confirms presence of supported organic functional groups (Fig. S2). The first weight loss at temperatures below 200°C, with an observed weight loss of 7.04%, is due to the removal of physically adsorbed solvent and surface hydroxyl groups and the evaporation of residual absorbed water.[27] The second weight loss occurs between 300 and 580°C, showing a weight loss of 6.1%, which may be related to the decomposition of (3-aminopropyl)triethoxysilane groups. The third weight loss between 580 and 730°C, with an observed weight loss of 5.3%, is related to the supported organic groups and Zr-oxide complex

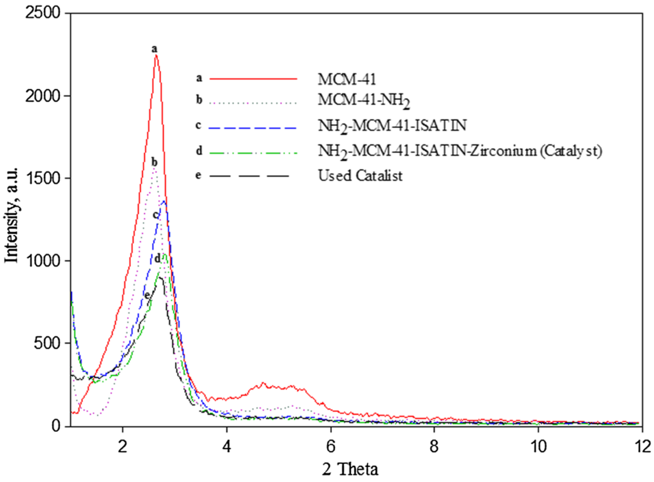


Figure 3. XRD patterns of (a) MCM-41, (b) MCM-41-NH_2, (c) Schiff base@MCM-41, (d) Zr-oxide@MCM-41 and (e) reused Zr-oxide@MCM-41.

grafting to the MCM-41 surface.[6] Finally, the weight loss above 400°C can be assigned mainly to the dehydroxylation of SiOH groups. The loading of the complex in Zr-oxide@MCM-41 can be calculated from inductively coupled plasma analysis, which confirms a loading of approximately 0.110 mmol g^{-1}.

FT-IR spectra of MCM-41, MCM-41-NH$_2$, Schiff base@MCM-41 and Zr-oxide@MCM-41 are shown in Fig. S3 in the supporting information. The vibrational band observed at 3433 cm^{-1} for MCM-41 is attributed to the silanol ν(OH) stretch. The bands at 1078 and 798 cm^{-1} correspond to the symmetric and asymmetric modes of the Si–O–Si bond stretching vibrations.[6] However, the appearance of new peak at 2980 cm^{-1} in the FT-IR spectrum of MCM-41-NH$_2$, which may be related to NH$_2$ bonds, confirms the anchoring of APTES on MCM-41. In the FT-IR spectra of Schiff base@MCM-41 and Zr-oxide@MCM-41, no bands are observed in the 2980 cm^{-1} region which would be associated with free amine group, indicating that isatin has been successfully condensed with supported APTES and grafted onto MCM-41-NH$_2$. Therefore, the disappearance of the 2980 cm^{-1} peak related to the NH$_2$ bonds confirms the formation of Schiff base@MCM-41. Also after imine formation the C=N stretching band appears at 1626 cm^{-1}. The FT-IR spectrum of the catalyst shows important bands from Zr-oxide@MCM-41. These are strong evidence that Zr-oxide complex is bonded to the surface of mesoporous MCM-41. The C=N stretching band shows an increase in frequency from 1626 to 1632 cm^{-1} due to complexation to metal ion.

The nitrogen adsorption–desorption isotherms of MCM-41, MCM-41-NH$_2$, Schiff base@MCM-41 and Zr-oxide@MCM-41 samples are illustrated in Figure 4. Based on the IUPAC classification, these materials display a typical type IV isotherm, which is characteristics of mesoporous material.[28] The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) for MCM-41, MCM-41-NH$_2$, Schiff base@MCM-41 and Zr-oxide@MCM-41 is 917, 512, 454 and 402 m^2 g^{-1}, respectively. That is, a decrease in S_{BET} is observed with functionalization. Physicochemical and structural parameters of the samples obtained from nitrogen isotherms are summarized in Table 1. The decrease in surface area of modified MCM-41 is attributed to the immobilization of APTES and Zr-oxide complex onto the mesoporous walls.

The wall thickness of MCM-41 is 2.05 nm, calculated using the following equation:[26]

$$\text{Wall thickness} = a_0 - D_{BJH} \qquad (2)$$

These results are strong evidence that Zr-oxide complex is bonded on the MCM-41.

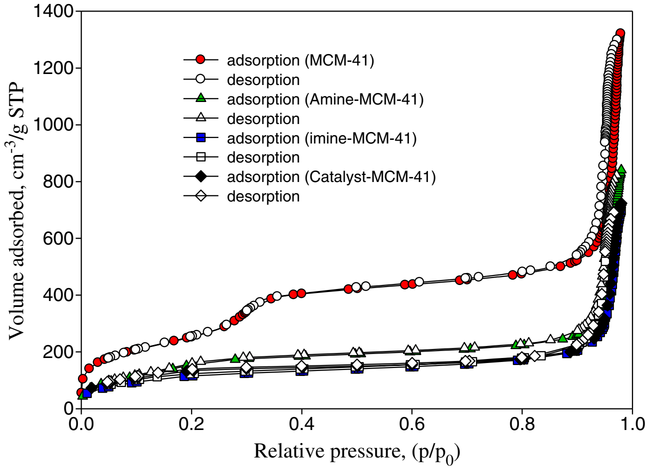


Figure 4. Nitrogen adsorption–desorption isotherms of (a) MCM-41, (b) MCM-41-NH$_2$, (c) Schiff base@MCM-41 and (d) Zr-oxide@MCM-41.

Table 1. Textural properties of synthesized materials obtained using nitrogen adsorption–desorption analysis

Sample	S_{BET} (m^2 g^{-1})	D_{BJH} (nm)	V_{Total} (cm^3 g^{-1})
MCM-41	917	2.44	0.979
Amine-MCM-41	512	2.26	0.758
Imine-MCM-41	454	1.41	0.177
Zr-imine-MCM-41	402	1.22	0.081

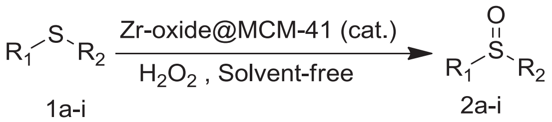
Catalytic Studies

As a first part of our organic study, the synthesized separable Zr-oxide complex immobilized on MCM-41 was tested for the oxidation of sulfides into sulfoxides using H$_2$O$_2$ as the oxidant at room temperature under solvent-free conditions (Scheme 2).

In order to optimize the reaction conditions, initially various solvents such as acetone, acetonitrile, ethanol, ethyl acetate, dichloromethane and *n*-hexane as well as solvent-free conditions were tested for the oxidation of dipropylsulfide using H$_2$O$_2$ as oxidant with Zr-oxide@MCM-41 as catalyst. Also, we evaluated the influence of varying the amount of catalyst on the oxidation of dipropylsulfide as a model compound under solvent-free conditions at room temperature (Table 2). As evident from Table 2, in the absence of catalyst the reaction is incomplete even after 24 h (Table 2, entry 7). The optimum amount of H$_2$O$_2$ (0.2 ml) in the presence of Zr-oxide@MCM-41 (10 mg, 1.64 × 10^{-4} mol%) at room temperature under solvent-free conditions is ideal for complete conversion of dipropylsulfide to dipropylsulfoxide (Table 2, entry 10).

We applied these optimized reaction conditions to various sulfide substrates to explore the catalytic activity of Zr-oxide@MCM-41. The various functional groups on the sulfides are well tolerated affording good to excellent yields of the corresponding sulfoxides. The results are summarized in Table 3. Moderate to good yields of the desired product are obtained using aliphatic, aromatic and cyclic sulphide substrates. Also, furfurylmethylsulfide affords good yield of furfurylmethylsulfoxide (Table 3, entry 3). To show the chemoselectivity of the presented protocol, a sulfide containing hydroxyl group was subjected to the oxidative reaction. The hydroxyl group remains intact during the conversion of sulfide to sulfoxide (Table 3, entry 9).

As a second part of our organic investigation towards the development of new methods for the coupling of thiols, we tested the catalytic activity of Zr-oxide@MCM-41 in the oxidative coupling of thiols into corresponding disulfides. Oxidative coupling of thiols into disulfides using H$_2$O$_2$ in the presence of this catalyst at room temperature in ethanol is shown in Scheme 3.



Scheme 2. Synthesis of Zr-oxide@MCM-41.

Table 2. Optimization of reaction conditions for the oxidation of dipropylsulfide (1 mmol) as a model compound at room temperature

Entry	Solvent	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Acetone	10	40	17
2	Acetonitrile	10	40	21
3	Ethanol	10	40	24
4	Ethyl acetate	10	40	35
5	CH_2Cl_2	10	40	38
6	*n*-Hexane	10	40	83
7	Solvent-free	—	24	15
8	Solvent-free	5	40	45
9	Solvent-free	7	40	56
10	Solvent-free	10	40	97
11	Solvent-free	20	40	98

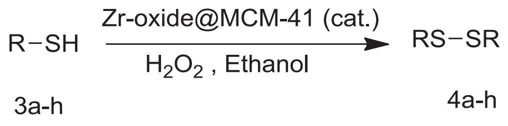
[a] Isolated yield.

Table 3. Oxidation of sulfides into sulfoxides using H_2O_2 catalysed by Zr-oxide@MCM-41 at room temperature under solvent-free conditions

Entry	Sulfide	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	Methylphenylsulfide	**2a**	300	98	Oil[29]
2	Ethyl 3-(methylthio) propanoate	**2b**	35	94	Oil[30]
3	2-((Methylthio)methyl) furan	**2c**	30	98	Oil[29]
4	Benzylmethylsulfide	**2d**	35	96	115–119[31]
5	Dibutylsulfide	**2e**	25	97	Oil[30]
6	Diethylsulfide	**2f**	20	91	Oil[32]
7	Tetrahydrothiophene	**2g**	25	95	Oil[29]
8	Dipropylsulfide	**2h**	40	97	Oil[29]
9	2-(Methylthio)ethanol	**2i**	30	94	Oil[30]

[a] Isolated yield.

The generality of this approach has been demonstrated by facile oxidative coupling of various thiols as summarized in Table 4. The disulfides are obtained in good to high yields. A variety of thiols including aromatic thiols (Table 4, entries 2–6), aliphatic thiols (Table 4, entries 7 and 8) and other thiols with different functional groups such as acidic group (Table 4, entries 5 and 8), amine group (Table 4, entry 4) and hydroxyl group (Table 4, entry 7) were successfully employed to prepare the corresponding disulfides in excellent yields. The hydroxyl group and other functional groups remain intact during the conversion of thiols into disulfides (Table 4, entry 7). This result indicates that the present protocol could be applicable to the chemoselective coupling of thiols in the presence of other functional groups. Therefore, the results reveal that this methodology is effective for a wide range of thiols.



Scheme 3. Zr-oxide@MCM-41-catalysed oxidation of sulfides into sulfoxides using H_2O_2.

Table 4. Oxidative coupling of thiols into disulfides using H_2O_2 catalysed by Zr-oxide@MCM-41 in ethanol at room temperature

Entry	Thiol	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	Phenylmethanethiol	4a	50	95	68–71[33]
2	4-Methylbenzenethiol	4b	30	99	36–38[16]
3	Naphthalene-2-thiol	4c	40	97	139–141[16]
4	2-Mercaptobenzoic acid	4d	35	96	285–290[16]
5	Benzenethiol	4e	30	98	56–58[16]
6	Benzo[*d*]thiazole-2-thiol	4f	20	99	170–172[33]
7	2-Mercaptoethanol	4g	30	97	Oil[16]
8	2-Mercaptoacetic acid	4h	40	90	Oil[16]

[a] Isolated yield.

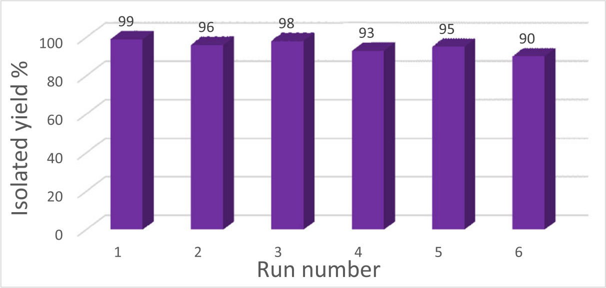


Figure 5. Reuse of catalyst in the oxidation of 4-methylthiophenol.

Reusability of Zr-oxide@MCM-41

To make the developed protocol more economical, the recyclability of the Zr-oxide@MCM-41 catalyst was studied for oxidative coupling of 4-methylthiophenol in ethanol. After completion of the reaction, the Zr-oxide@MCM-41 catalyst was separated by simple filtration. The catalyst was then washed with ethyl acetate to remove traces of organic compounds, dried and subjected to the next cycle. The catalyst could be reused for up to six consecutive cycles without significant loss of its catalytic efficiency (Fig. 5). The recovered catalyst after one use shows a decrease in XRD peak intensity but no changes in the mesostructure and it still has ideal mesoporosity (Fig. 3).

Conclusions

A simple, efficient and environmentally benign method has been developed for the oxidation of sulfides to sulfoxides and for the oxidative coupling of thiols into their corresponding disulfides using Zr-oxide@MCM-41 having high catalytic activity. The notable advantages of these methods are easy-to-handle environmentally friendly reagents, cheap and chemically stable oxidant, operational simplicity, practicability, good to high yields of products in a short time and inexpensive reagents. More important, the catalyst can be easily recovered using simple filtration and reused several times without significant loss of its catalytic activity.

Acknowledgement

The authors thank the research facilities of Ilam University, Ilam, Iran, for financial support of this research project.

References

[1] S. Shylesh, V. Schunemann, W. R. Thiel, *Angew. Chem. Int. Ed.* **2007**, *49*, 3428.
[2] E. Lovell, Y. Jiang, J. Scott, F. Wang, Y. Suhardja, M. Chen, J. Huang, R. Amal, *Appl. Catal. A* **2014**, *473*, 51.
[3] D. J. Thompson, Y. Zhang, T. Ren, *J. Mol. Catal. A* **2014**, *392*, 188.
[4] D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed.* **2005**, *44*, 7852.
[5] B. Boukoussa, S. Zeghada, G. B. Ababsa, R. Hamacha, A. Derdour, A. Bengueddach, F. Mongin, *Appl. Catal. A* **2015**, *489*, 131.
[6] M. Hajjami, F. Ghorbani, F. Bakhti, *Appl. Catal. A* **2014**, *470*, 303.
[7] A. M. B. Furtado, Y. Wang, T. G. Glover, M. D. Levan, *Micropor. Mesopor. Mater.* **2011**, *142*, 730.
[8] N. V. Roik, L. A. Belyakova, *J. Solid State Chem.* **2013**, *207*, 194.
[9] Y. Huang, W. Hao, G. Ding, M. Z. Cai, *J. Organometal. Chem.* **2012**, *715*, 141.
[10] N. Cuello, V. Elías, M. Crivello, M. Oliva, G. Eimer, *J. Solid State Chem.* **2013**, *205*, 91.
[11] N. Wu, W. Zhang, B. Li, C. Han, *Micropor. Mesopor. Mater.* **2014**, *185*, 130.
[12] P. Oliveira, A. Machado, A. M. Ramos, I. Fonseca, F. M. Braz Fernandes, A. M. Botelho do Rego, J. Vital, *Micropor. Mesopor. Mater.* **2009**, *120*, 432.
[13] R. A. Khan Rao, S. Singh, B. R. Singh, W. Khan, A. H. Naqvi, *J. Environ. Chem. Eng.* **2014**, *2*, 199.
[14] T. Zhang, Y. Q. Deng, W. F. Zhou, C. T. Au, S. F. Yin, *Chem. Eng. J.* **2014**, *240*, 509.
[15] X. B. Li, Z. J. Li, Y. J. Gao, Q. Y. Meng, S. Yu, R. G. Weiss, G. H. Tung, L. Z. Wu, *Angew. Chem. Int. Ed.* **2014**, *53*, 2085.
[16] A. Ghorbani-Choghamarani, G. Azadi, B. Tahmasbi, M. Hadizadeh-Hafshejani, Z. Abdi, *Phosphorus Sulfur Silicon Relat. Elem.* **2014**, *189*, 433.
[17] H. B. Jeon, K. T. Kim, S. H. Kim, *Tetrahedron Lett.* **2014**, *55*, 3905.
[18] A. Shaabani, A. H. Rezayan, *Catal. Commun.* **2007**, *8*, 1112.
[19] B. Sreedhar, P. Radhika, B. Neelima, N. Hebalkar, A. K. Mishra, *Catal. Commun.* **2008**, *10*, 39.
[20] G. P. Romanelli, P. I. Villabrille, C. V. Cáceres, P. G. Vázquez, P. Tundo, *Catal. Commun.* **2011**, *12*, 726.
[21] L. Villalobos, T. Ren, *Inorg. Chem. Commun.* **2013**, *28*, 52.
[22] B. V. Tamhankar, *Int. J. Res. Org. Chem.* **2014**, *4*, 4.
[23] S. Thurow, V. A. Pereira, D. M. Martinez, D. Alves, G. Perin, R. G. Jacob, E. J. Lenardão, *Tetrahedron Lett.* **2011**, *52*, 640.
[24] A. Rostami, B. Tahmasbi, F. Abedi, Z. Shokri, *J. Mol. Catal. A* **2013**, *378*, 200.
[25] C. C. Torres, C. H. Campos, J. L. G. Fierro, P. Reyes, D. Ruiz, *J. Mol. Catal. A* **2014**, *392*, 321.
[26] D. Zhao, J. Feng, Q. Huo, J. L. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
[27] A. Pajzderska, M. A. Gonzalez, J. Mielcarek, J. Wąsick, *J. Phys. Chem. C* **2014**, *118*, 23701.
[28] A. Mathew, S. Parambadath, S. S. Park, C. S. Ha, *Micropor. Mesopor. Mater.* **2014**, *200*, 124.
[29] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, *Catal. Commun.* **2015**, *60*, 70.
[30] M. A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi, S. Jafari, *Catal. Commun.* **2008**, *9*, 1739.
[31] C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. Deng, *Green Chem.* **2009**, *11*, 1401.
[32] A. Bayat, M. Shakourian-Fard, M. M. Hashemi, *Catal. Commun.* **2014**, *52*, 16.
[33] A. Ghorbani-Choghamarani, M. Nikoorazm, H. Goudarziafshar, A. Shokr, H. Almasi, *J. Chem. Sci.* **2011**, *123*, 453.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.