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A highly efficient, green, rapid, and chemoselective oxidation of sulfur containing compounds in presence of MCM-41@creatinine@M (M= La and Pr) mesostructured catalyst under neat conditions

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In the present study, we report the synthesis of two green recoverable catalysts by covalent linking of creatinine La and Pr complexes on MCM-41 mesostructured via commercially available materials and simple and inexpensive procedure. These heterogeneous catalysts were characterized by Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, scanning electron microscopy, N_2 adsorption and desorption, inductively coupled plasma optical emission spectroscopy and thermal gravimetric analysis. The obtained mesostructures act as active and reusable catalysts for oxidation of sulfides and oxidative coupling of thiols under neat conditions. More importantly, significant practical advantages of this environment-friendly process are high efficiency, good reaction times, convenient recovery and reusability for several times without any significant loss of activity.

1 Introduction

During the recent years, ‘‘Green Chemistry’’ has received considerable importance in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents [1]. Therefore, significant progress has been made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents in order to increasing attention to problems of chemical pollution and resource depletion that minimize the use and generation of hazardous substances [2-4] .In this regard, the heterogeneous catalysts has attracted a great deal of attention in recent times, since the potential advantages of these materials such as simplified recovery and providing improved reusability in the designed systems can have positive environmental effects. Indeed, the use of reusable heterogeneous catalysts is important issues in organic synthesis because of their chemical, economic, environmental, and industrial aspects [5-9]. Despite the widespread applications of the heterogeneous catalysts, these catalysts have lower catalytic activities than their hemogeneous counterparts. To overcome these drawbacks, in order to combine the advantages of both homogeneous and heterogeneous catalysis, immobilization of homogeneous catalysts on heterogeneous nanomaterials can use as an efficiently bridge the gap between homogeneous and heterogeneous catalysis [10-13]. Up to now, a diverse range of supports such as zeolite, carbon nanotubes, graphene, heteropolyacids, ionic liquids or some polymers have been developed for the construction of organic compounds and synthetic intermediates, which most of these supports exhibit disadvantages such as expensive, use of atmosphere or high temperature for calcination or preparation, unstable and tedious recycling procedures [14-16]. In the recent years, considerable research was paid towards development of mesoporous nanoparticles, especially mesoporous silica nanoparticles (MSNs) with a diameter below 200 nm as immobilized support. It should be noted that the mesoporous silica materials with nano-sized pores and controllable porous structure and pore volume can use as a suitable catalyst support for organic transformations. Also, silica mesoporous nanocomposite in particular MCM-41 was represented several significant features in comparison with its heterogeneous catalysts [17-20]. Indeed, among the different types of mesoporous supports, mesoporous MCM-41 has excellent properties such as high activity, uniform pore structure, excellent stability (chemical and thermal), good accessibility, lager surface area, associated with high thioresistance for the hydrogenation of aromatics found in diesel fuels, and inert environment for immobilization of transition metal nanoparticles [21-25]. It is noteworthy that the ability to stabilize reactive metal ions in mesoporous silica framework due to their low toxicity and low cost has made them unique in heterogeneous catalysis. The walls of the porous system of MCM-41 can be easily modified with anchoring of different ligands into the hexagonal channels [26,27]. On the other hand, mesostructured catalysts can be used as recoverable and reusable heterogeneous catalysts in the oxidation of sulfides, oxidative coupling of thiols [28-30]. Disulfides and sulfoxides, among organic sulfur compounds, have attracted great interest because of the large number of applications, such as precursors or intermediates in the synthesis of natural products and valuable physiologically and pharmacologically active molecules as well as important integral and supplementary parts in many pharmaceutical and biological

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active molecules such as cystine, DTNB (Ellman's reagent or 5,50-dithio-bis(2-nitrobenzoic acid), omeprazole and fipronil [31-33]. In the present work, we report synthesis of La and Pr complex supported on mesoporous silica by anchoring of creatinine on the wall of functionalized MCM-41, then reacted with La $(NO_3)_2.6H_2O$ and $Pr(NO_3)_2.5H_2O$, respectively. On the other hand, the prepared catalysts were investigated for oxidation of sulfides and oxidative coupling of thiols, which exhibit a high stability and catalytic activity in these reactions. High surface area, convenient recovery and reusability for several times without any significant loss of activity, the use of a commercially available, eco-friendly, cheap and chemically stabile reagents, good reaction times and simple practical methodology; makes this protocol both attractive and economically viable.

2 Results and discussion

2.1 Catalyst preparation

Following the method reported on application of heterogeneous catalyst in for oxidation of sulfides and oxidative coupling of thiols [34-37], we decided to prepare two novel and green heterogeneous catalysts for this purpose. Initially, MCM-41 particles were prepared according to a previous report by Hajjami et al [38] and subsequently coated with 3-chloropropyltrimethoxysilane (CMTS). Also, immobilized creatinine ligand on mesostructured MCM-41 was successfully synthesized by using the surface modification strategy as depicted in Scheme 1. Then, MCM-41@creatinine@La and MCM-41@creatinine@Pr catalysts were prepared using stable interaction between the N and O atoms of creatinine and M (M=La and Pr). The proposed structure is designed according to recently reported procedure [39]. It should be noted that creatinine was chosen as a green, available, cheap and readily available chelating ligand.

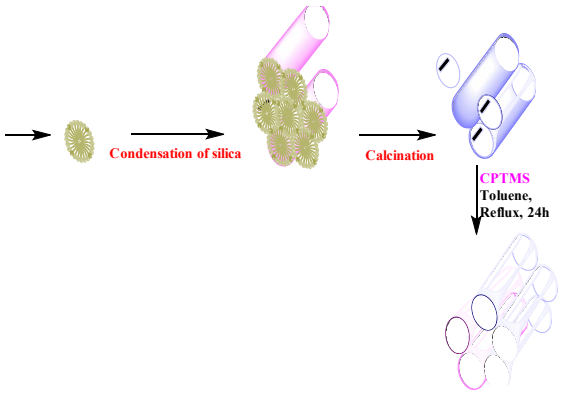

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Table 1

Texture parameters obtained from nitrogen adsorption studies.

Sample	S_{BET} (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@creatinine@La	584.79	1.01	0.673
MCM-41@creatinine@Pr	620.22	1.21	0.714

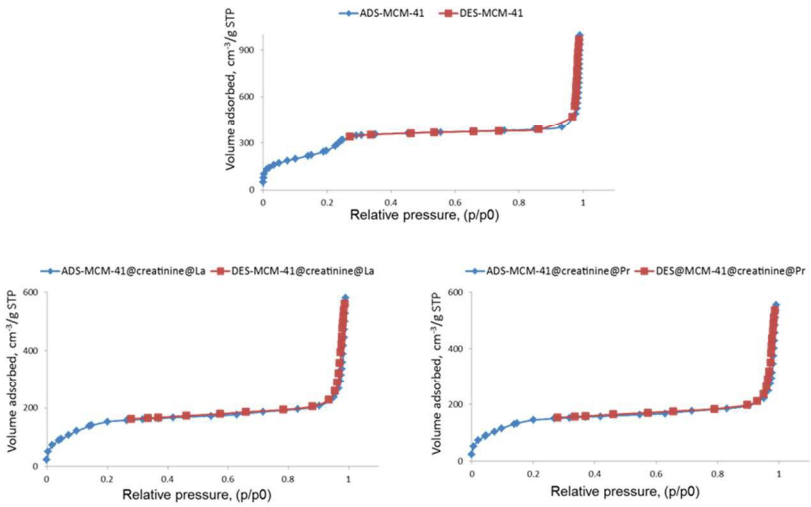

Fig. 2 Nitrogen adsorption/desorption isotherms of MCM-41 (a), MCM-41@creatinine@La and MCM-41@creatinine@Pr.

2.2.3 X-ray diffraction

The crystalline structures of the MCM-41, and MCM-41@creatinine@La and MCM-41@creatinine@Pr were determined by powder X-ray diffraction (XRD). In all materials, well-resolved peaks with very intense diffraction peaks indicated that can be indexed as (100), (110), and (200) reflections attributed to the presence a hexagonal space group symmetry P6mm. After the immobilization of La and Pr complexes on the wall of functionalized MCM-41, an overall decrease in diffraction (100), (110) and (200) reflections was noticed that is due to the difference in the scattering contrast of the pores and the walls of nanochannels of MCM-41 (Fig. 3). Also, the peak shifting at (100) plane can be observed after immobilization of La and Pr complexes on the inner channel pores. Therefore, it can be concluded that the formation of the catalyst has taken place preferentially inside the pore system of the MCM-41.

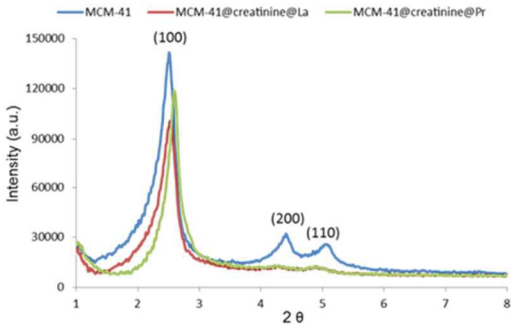

Fig. 3 Small angle XRD patterns of MCM□41 (blue), MCM□41@creatinine@La (red) and MCM□41@creatinine@Pr (green).

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2.2.4. FT-IR spectroscopy

Fig.4 shows the FT-IR spectra of MCM-41, MCM-41@Cl, MCM-41@creatinine, MCM-41@creatinine@La and MCM-41@creatinine@Pd in the 400–4000 cm^{-1}. It should be mentioned that the Fourier transform infrared spectroscopy is helpful to examine the synthesis process. The presence of peaks at 481, 820 and 1079 to 1225 cm^{-1} was most probably due to the symmetric and asymmetric stretching vibrations of framework and terminal Si–O groups (Fig. 1a). Also, the presence of peaks at 2950 and 2850 cm^{-1} was most probably due to the C–H stretching vibrations (Fig. 4b). The C-N and C=O stretching peaks at 1250 and 1710 cm^{-1} indicate that the surface of silica is successfully modified by creatinine ligand (Fig 4c). On the basis of these observations, Fig. 1d and 1e indicate that the bending vibration absorption band of N–H is shifted to lower wavenumbers, which is perhaps due to the robust interaction between the N groups of La and Pr complexes on the MCM-41.

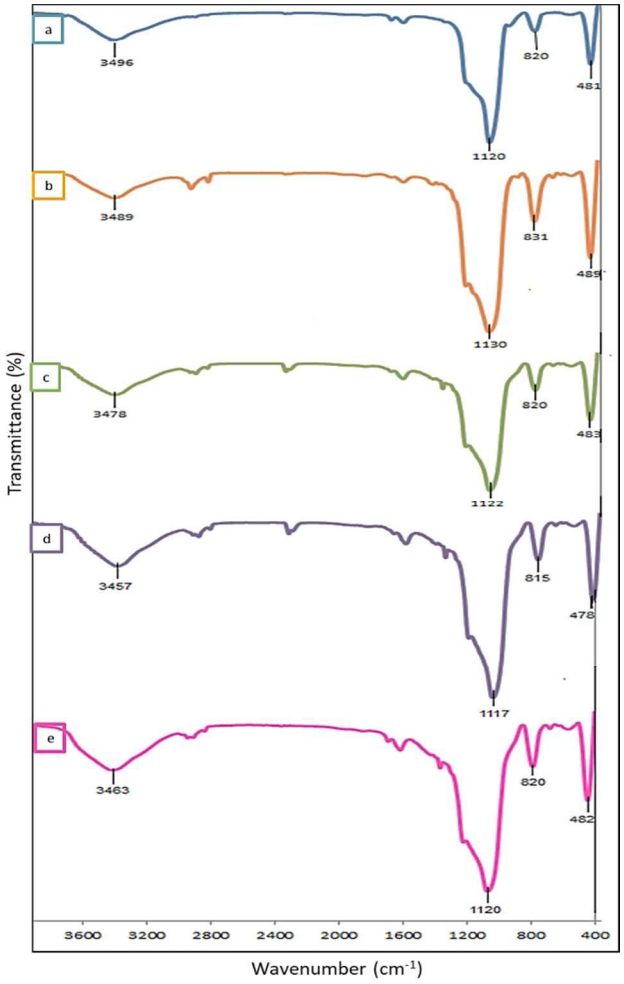

Fig. 4 FT-IR spectrum for bare of MCM-41 (a), MCM-41@Cl (b), MCM-41@creatinine (c), MCM-41@creatinine@La (d) and MCM-41@creatinine@Pr (e).

2.2.5 Scanning electron microscopy

Fig. 5 shows the FESEM images of the MCM-41 (a), MCM-41@creatinine@La (b) and MCM-41@creatinine@Pr (c) for investigation of the surface morphology of the obtained nanostructure. According to the FESEM images, prepared samples were made up of quite homogeneous and uniform spherical particles and no significant changes in the morphology occurred after anchoring of lanthanum and praseodymium complexes onto the surface of mesoporous MCM-41 silica.

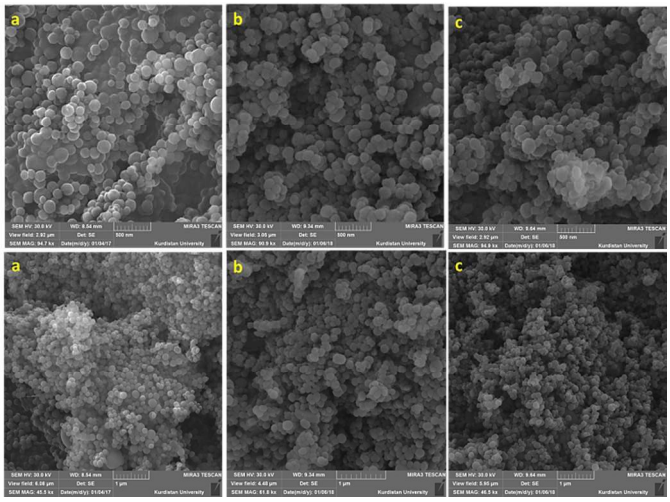

Fig. 5 FESEM images of MCM-41 (a), MCM-41@creatinine@La (b) and MCM-41@creatinine@Pd (c) at 500 nm (top) and 1 µm (down).

It should be noted that the immobilization of La and Pr complexes on mesoporous MCM-41 were confirmed through the presence of N, O, C, Si, La and Pr species in EDX analysis of these synthesized catalyst (Fig. 6). Also, the exact amount of La and Pr loaded on surface of modified mesoporous silica are found to be 0.46 and 0.41 mmol g^{-1} using the ICP atomic emission spectroscopy technique. More importantly, interpretations made on the basis of ICP results are supported by the EDX data.

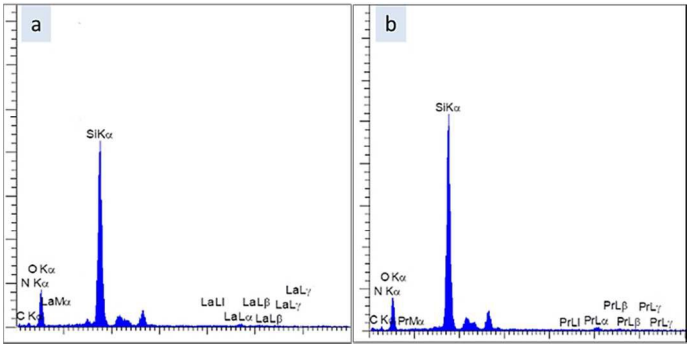

Fig. 6 EDX spectrum of MCM-41@creatinine@La (a) and MCM-41@creatinine@Pd (b).

2.3 Catalytic studies

After characterization of the MCM-41@creatinine@La (I) and MCM-41@creatinine@Pr (II), we examined the catalytic activity of these catalysts as efficient, stable, recyclable and commercially viable catalysts in the oxidation of sulfides to sulfoxides (Scheme 2) and oxidative coupling of thiols to disulfides (Scheme 4) in the present of H_2O_2 (30%) as oxidant under neat conditions at room temperature. In order to find the best reaction conditions, the oxidation of methylphenyl sulfide using H_2O_2 (30%) was selected as a model compound in the presence of different amounts of MCM-

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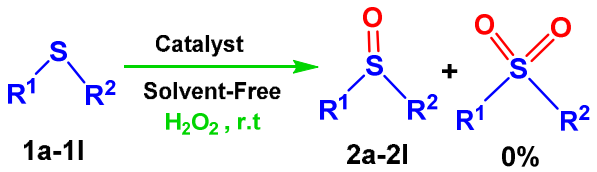
41@creatinine@Pr in various solvents as well as solvent-free conditions. The results of observation are summarized in Table 2. In initial experiments, the solvent effect was examined that good yields were obtained in solvent-free. Then, the amount of catalyst was also examined, and 0.005 g of MCM-41@creatinine@Pr was found to be optimal. Also, it was found that a lower yield was observed when the amount of the catalyst was decreased. Finally, the amount of H_2O_2 was examined that optimization condition were obtained in 0.4 mL H_2O_2 for in the synthesis of methylphenyl sulfoxide. More importantly, because of mild conditions of described heterogeneous systems, there is no overoxidation to sulfone for oxidation of sulfides.



Scheme 2. Oxidation of sulfides to the corresponding sulfoxides.

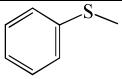
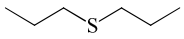
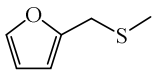
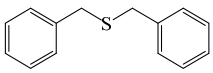
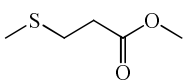
Table 2 Optimization of reaction conditions for the oxidation of methylphenyl sulfide in the presence of MCM-41@creatinine@Pr using H_2O_2.

Entry	Catalyst (mg)	Solvent	H_2O_2 (mL)	Time (min)	Yield (%)[a]
1	5	EtOH	0.4	35	63
2	5	Ethyl acetate	0.4	35	42
3	5	Acetonitrile	0.4	35	38
4	5	Solvent-Free	0.4	35	94
5	4	Solvent-Free	0.4	35	73
6	6	Solvent-Free	0.4	35	95
8	3	Solvent-Free	0.4	35	49
9	5	Solvent-Free	0.5	35	95
10	5	Solvent-Free	0.3	35	63
11	0	Solvent-Free	0.4	10 h	Trace

[a] Isolated yield.

As it is evident from Tables 3, under the obtained optimized conditions, the various sulfides including several of functional groups were successfully employed to prepare the corresponding sulfoxides in the presence of MCM-41@creatinine@La (I) and MCM-41@creatinine@Pr (II) as catalyst. All products are obtained in the short reaction time and in good to excellent yields. Also, we found that the coupling reaction yield and time was susceptible to type of catalyst. It is important to note that these results were obtained by comparing the effect of prepared catalysts trough the oxidation of sulfide to corresponding sulfoxides. As listed in Table 3, the effect of catalyst was carefully investigated and the best results were obtained in the presence of MCM-41@creatinine@Pr. The obtained results are summarized in table 3.

Table 3 Oxidation of sulfides to the sulfoxides in the presence of prepared catalysts.

Entry	Substrate	Product	Time (min)		Yield (%)[a]		TOF (h^{-1})	
			Cat (I)	Cat (II)	Cat (I)	Cat (II)	Cat (I)	Cat (II)
1		**2a**	40	35	92	94	600	786.06
2		**2b**	55	50	96	95	455.34	556.1
3		**2c**	35	35	95	97	708.07	722.98
4		**2d**	45	35	87	91	504.35	760.97
5		**2e**	55	50	91	93	431.62	544.39

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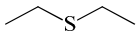
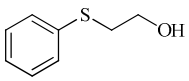
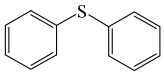
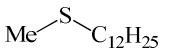
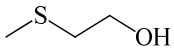
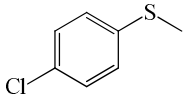
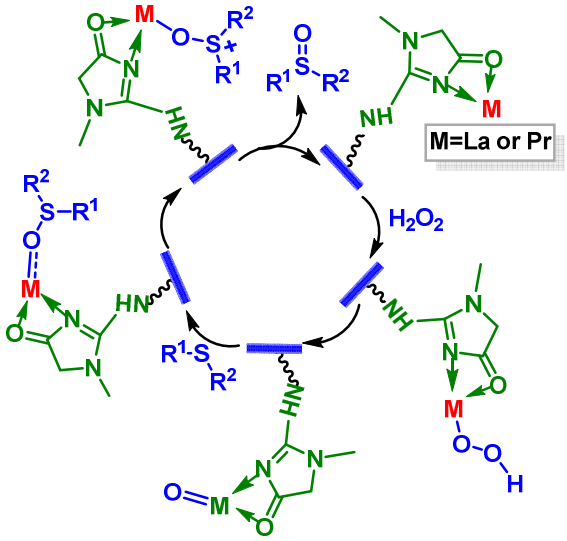
6		**2f**	5	5	99	96	5165.22	5619.5
7		**2g**	85	80	89	92	273.15	336.58
8		**2h**	55	35	96	91	455.34	760.97
9		**2i**	50	45	91	92	474.78	598.37
10		**2j**	75	70	93	95	323.48	397.21
11		**2k**	75	75	87	90	313.04	351.22
12		**2l**	70	60	93	90	346.58	439.02

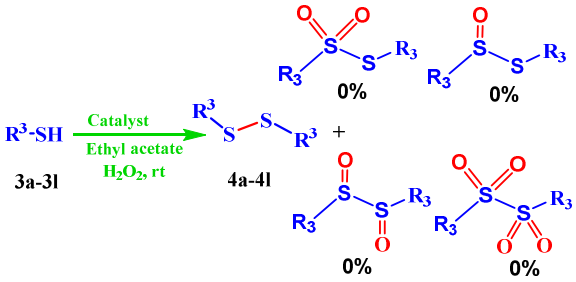
[a]Isolated yield

Finally, a plausible reaction mechanism for oxidation of sulfides in the presence of catalyst is proposed on the basis of the literatures (Scheme 3) [8].



Scheme 3 Proposed mechanism for the oxidation of sulfides presence of catalyst.

As the second part of our organic study, we also studied the synthesis of disulfide compounds from reaction of 4-methylbenzenethiol (1 mmol) and H_2O_2 as a model reaction. Hence, the reaction conditions in the synthesis of disulfide derivatives were optimized for above mentioned reaction under the influence of different amounts of MCM-41@creatinine@Pr as catalyst in various solvents as well as solvent-free conditions. It was observed that 0.005 g MCM-41@creatinine@Pr catalyst in the presence of 0.4 mL H_2O_2 in EtOH at room temperature was found to be ideal reaction conditions for the oxidative coupling of 4-methylbenzenethiol. Also, because of mild conditions of described heterogeneous systems, all the reactions take place with total selectivity. The results of this study are summarized in Table 4.



Scheme 4. Oxidative coupling of thiols into disulfides.

Table 4 Optimization of oxidative coupling of 4-methylthiophenol using MCM□41@creatinine@Pr under various conditions.

Entry	Catalyst (mg)	Solvent	H_2O_2 (mL)	Time (min)	Yield (%)[a]
1	5	Solvent-Free	0.4	40	71
2	5	Ethyl acetate	0.4	40	47
3	5	Acetonitrile	0.4	40	58
4	5	EtOH	0.4	40	97
5	4	EtOH	0.4	40	78
6	3	EtOH	0.4	40	48
7	5	EtOH	0.5	40	97
8	6	EtOH	0.4	40	98
9	5	EtOH	0.3	40	77
10	0	EtOH	0.4	10 h	Trace

[a] Isolated yield.

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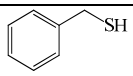
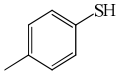
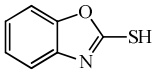
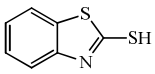
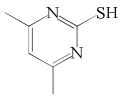
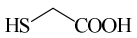
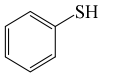
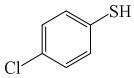
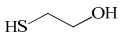
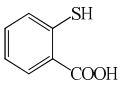
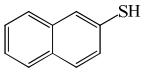
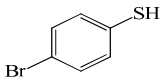
Then, under the optimized reaction conditions, we shown the generality of this approach by a facile oxidation of various sulfides. As shown in Table 5, a variety of sulfides with different functional groups were successfully employed to prepare the corresponding sulfoxides. It can be seen that the sulfoxides were obtained in high yields in the presence of MCM-41@creatinine@La (I) and MCM-41@creatinine@Pr (II) as catalyst. It should be noted that the effect of catalyst was carefully investigated and the best results were obtained in the presence of MCM-41@creatinine@Pr. MCM□41@creatinine@La and MCM□41@creatinine@Pr were acted as Lewis acids. Pr and La were metals in the 4f block lanthanide series. More importantly, MCM-41@creatinine@Pr is a stronger Lewis acid than MCM□41@creatinine@La.

Therefore, based on theoretical principles and proposed mechanisms in Scheme 3 and 5, the catalytic activity of MCM-41@creatinine@Pr is better than the MCM-41@creatinine@La.

Table 5 Oxidation of sulfides to the sulfoxides in the presence of prepared catalysts.

Entry	Substrate	Product	Time (min)		Yield (%)[a]		TOF (h^{-1})	
			Cat (I)	Cat (II)	Cat (I)	Cat(II)	Cat(I)	Cat(II)
1		**2a**	65	60	96	91	3 85.28	443.9
2		**2b**	50	45	95	97	495.65	630.89
3		**2c**	35	35	91	95	678.26	794.42
4		**2d**	45	40	97	92	562.32	637.17
5		**2e**	55	50	93	91	441.1	532.68
6		**2f**	55	45	88	87	417.39	565.85
7		**2g**	35	30	90	94	670.81	917.07
8		**2h**	50	45	95	87	495.65	565.85
9		**2i**	65	60	85	90	341.14	439.02
10		**2j**	40	40	91	93	593.48	680.49
11		**2k**	50	45	93	90	485.22	585.36
12		**2l**	60	55	90	91	391.3	484.26

[a]Isolated yield.

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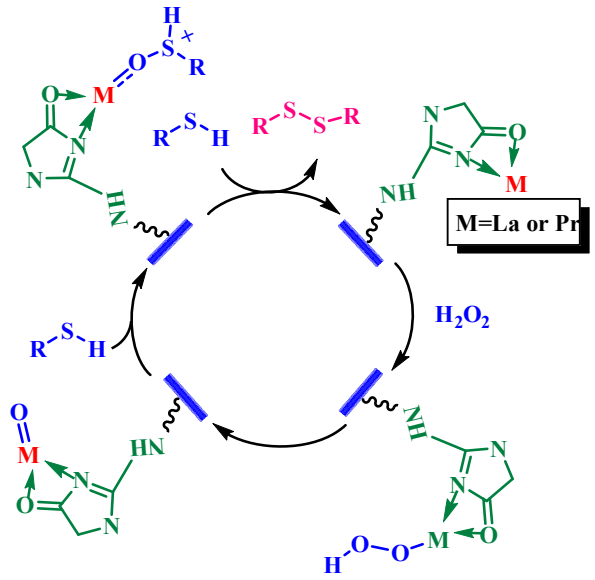
It should be mentioned that proposed mechanism for this process using H_2O_2 as oxidant in the presence catalyst is outlined in Scheme 5 [8].



Scheme 5. Proposed mechanism for oxidative coupling of thiols in presence of catalyst.

3.4 Reusability of the catalyst

One of outstanding advantages of these heterogeneous catalysts over its homogeneous counterpart is its easy separation from reaction media and the possibility of reusing the catalyst after reaction. Therefore, in continuation of our studies in the introduction of novel and green catalysts, the reusability of described catalysts was examined using the synthesis of methylphenyl sulfoxide and 1,2-di(naphthalen-2-yl)disulfane in after several reaction cycles. In this procedure, after completion of each reaction, the recovered catalyst was washed with ethyl acetate to remove residual product and the catalyst reused for next reactions for several times without any significant loss of its catalytic activity or metal leaching (Fig.7).

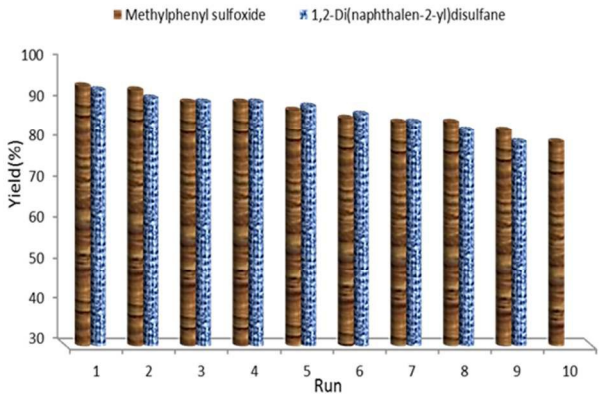


Fig. 7 Reusability of MCM-41@creatinine@Pr in the oxidation of methyl phenyl sulfide and MCM-41@creatinine@La in oxidative coupling of 2-naphthalenethiol.

3.5 Catalyst leaching study

Finally, using ICP-OEIS technique, the exact amount of metal leaching was studied by checking the amount of metal loading on modified MCM-41 before and after recycling of the catalyst. Based on ICP-OEIS analysis of the prepared catalysts, the recycled MCM-41@creatinine@Pr in the oxidation of methyl phenyl sulfide and the recycled MCM-41@creatinine@La in oxidative coupling of 2-naphthalenethiol after several times recycling is 0.31 and 0.28 mmol g^{-1}, respectively. Also, the oxidative of methyl phenyl sulfide in the presence of MCM-41@creatinine@Pr and oxidative coupling of 2-mercaptoethanol in the presence of has been investigated to perform hot filtration experiment under optimized reaction conditions. In the oxidation of methylphenyl sulfide and oxidative coupling of 2-mercaptoethanol, we found the yield of product under optimized conditions in half time of the reaction that it was 67 and 58 %, respectively. Then, described reactions were repeated and in half time of the reaction, the catalysts were separated from reaction mixture and allowed the iltrate to react further under identical reaction conditions. The yield of reaction in this stage was 70 and 62 % the oxidation of methylphenyl sulfide and oxidative coupling of 2-mercaptoethanol, respectively, that confirmed the leaching of metal hasn't been occurred.

3.6 Comparison of the catalyst

To show the merit of prepared catalysts in comparison with other reported catalysts, the activity of described catalysts in comparison with the best of the reported data in the literatures was evaluated (Table 6). It is observed that all synthesized mesostructured catalysts showed good reaction time and better performance than the well-known catalyst from the literature as out lined in the Table 6. In these nanohybrid robust catalysts represents the attractive features including operational simplicity, facile synthesis, environmental friendliness, and recyclability of the catalyst by simple filteration as well as the ability to tolerate a wide variety of substitutions in the reagents.

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Table 6 Comparison results of prepared catalysts with other catalysts in the oxidation reaction**.**

Entry	Substrate	Catalyst	Time (h)	Yield (%)	TOF (h^{-1})	Refs.
1	methylphenyl sulfide	Ni-complex-boehmite	1.58	98	213.43	[40]
3	methylphenyl sulfide	Ru^{II}(TMP)(CO)	1.5	90	270	[41]
4	methylphenyl sulfide	SiO_2–2-ImSiO_2–2-Im	2.5	86	22.8	[42]
5	methylphenyl sulfide	Mn(III)–salphen	0.53	95	178.2	[43]
6	methylphenyl sulfide	MCM-41	1	23	-	This work
7	methylphenyl sulfide	MCM-41@creatinine	1	14	-	This work
8	methylphenyl sulfide	creatinine@La	0.68	89	579.9	This work
9	methylphenyl sulfide	creatinine@Pr	0.61	90	745.4	This work
10	methylphenyl sulfide	MCM-41@creatinine@La	0.66	92	600	This work
11	methylphenyl sulfide	MCM-41@creatinine@Pr	0.58	94	786.06	This work
12	4-Methylbenzenthiol	Ni-SMTU@boehmite	1.33	94	53.95	[8]
13	4-Methylbenzenthiol	Fe_3O_4-Adenine-Zn	1.5	99	235.71	[13]
14	4-Methylbenzenthiol	Fe NPs @ SBA-15	0.75	94	29.19	[45]
15	4-Methylbenzenthiol	Fe_3O_4/salen of Cu(II)	0.25	97	165.12	[46]
16	4-Methylbenzenthiol	MCM-41	1	19	-	This work
17	4-Methylbenzenthiol	MCM-41@creatinine	1	10	-	This work
18	4-Methylbenzenthiol	creatinine@La	0.80	92	472.5	This work
19	4-Methylbenzenthiol	creatinine@Pr	0.71	93	609.1	This work
20	4-Methylbenzenthiol	MCM-41@creatinine@La	0.83	95	495.65	This work
21	4-Methylbenzenthiol	MCM-41@creatinine@Pr	0.66	97	630.89	This work

[a] Isolated yield.

3 Conclusions

In this work, we reported two novel and green recoverable heterogeneous catalytic system by simple and inexpensive procedure. Then, these nanohybrids were carefully characterized by FT-IR, XRD, TGA, BET, SEM and ICP-OES techniques. It was be found that heterogeneous catalysts could be easily separated by applying a simple filteration and reused several consecutive runs without appreciable change in its catalytic activity. These mesostructures were exhibited enhanced catalytic performance compared to other similar reported catalysts, and has been successfully utilized for the oxidation of sulfur containing compounds using urea hydrogen peroxide (UHP) under condition under mild conditions. More importantly, these nanohybrid robust catalysts has excellent advantages such as high surface area, the use of a commercially available, chemically stabile reagents, eco-friendly, low cost, operational simplicity, good reaction times and high efficiency in the above-mentioned reactions.

4 Experimental

4.1 Materials

Tetraethylorthosilicate (TEOS), cetyl trimethylammonium bromide (CTAB), creatinine dipropylsulfide, diethylsulfide, dibenzylsulfide, benzylphenylsulfide, tetrahydrothiophene, dodecyl methylsulfide, methylphenylsulfide, 2-(phenylthio)ethanol, diphenyl sulfide, benzo[d]thiazole-2-thiol, benzyl mercaptan, 4-methylbenzenethiol, naphthalene-2-thiol, 2-mercaptopyridine, thiophenol, benzo[d]oxazole-2-thiol, 2-mercaptoacetic acid, 4-bromothiophenol, 3-chloropropyltrimethoxysilane (CPTMS), triethylamine, H_2O_2 (33 %), La $(NO_3)_3.6H_2O$ and $Pr(NO_3)_3.5H_2O$ and all solvents used in this work are purchased from Merck, Flucka or Aldrich and used without further purification.

4.2 Measurement

Infrared sample spectra were examined on a Bruker VERTEX 80 v model using the KBr pellets in the range of 400-4000 cm-1.The elemental analysis of the samples was done by Energy-dispersive X-ray spectroscopy (EDAX, TSCAN). Measuring the Amount of metal in synthesized nanostructure was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES). Powder X-ray diffraction (XRD) measurements were done using Co radiation source with a wavel length = 1.78897 Å, 40 kV at various points. Thermogravimetric analysis (TGA) was carried out on Shimadzu DTG-60 instrument in different temperatures. The surface morphology of synthesized nanostructural material

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were investigated by measuring SEM using FESEM-TESCAN MIRA3.

4.3 Preparation of MCM-41@creatinine

Mesoporous MCM-41 was synthesized through the sol-gel method by previous report by Hajjami et al [38]. Cetyltrimethylammonium bromide (CTAB), as structure directing template agent, was dissolved in a solution containing 3.5 mL of NaOH solution (2 M) and deionized water (480 mL) at 80 °C under stirring condition. After TEOS (5 mL) as the silica source was gradually added to the solution and the mixture stirred at the same temperature for 2 h. Finally, the solid product wasrecovered by filtration and washed with deionized water and dried in an oven at 60 ˚C followed by calcination at 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. Additionally, the reaction mixture was filteration and washed with n-hexane and dried under vacuum to obtain chlor-functionalized MCM-41 (MCM-41-Cl). Then, creatinine (0.226 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.

4.4 Preparation of MCM-41@creatinine@La

The as-synthesized MCM-41@creatinine mesostructured (1 g) was dispersed in absolute ethanol (30 mL). Then $La(NO_3)_3.6H_2O$ (1.08 g) was added, and the mixture was boiled under reflux for 24 h and cooled at room temperature. The product was collected by simple filteration, washed several times with ethanol and dried under vacuum at room temperature to obtain MCM-41@creatinine@La.

4.5 Preparation of MCM-41@creatinine@Pr

Furthermore, the obtained Preparation of MCM-41@creatinine (1 g) as support was dispersed in 30 mL of ethanol, and then $Pr(NO_3)_3.5H_2O$ (1.04 g) was added to the reaction mixture and this mixture was refluxed for 16 h. Finally, the reaction mixture separated by simple filteration and washed with absolute ethanol to remove the unattached substrates, and then dried at room temperature to obtain MCM-41@creatinine@Pr.

4.6 General procedure for the preparation of sulfoxides

In this study, to a mixture of sulfide (1 mmol) and H_2O_2 (0.4 mL) under solvent-free condition, 0.005 g catalyst was added; and the mixture was stirred at room temperature an appropriate time. After the reaction was completed (monitored by TLC), the catalyst separated by the filtration process and the residual mixture was extracted with ethyl acetate. Finally, pure sulfoxides were obtained by removing solvent.

4.7 General procedure for the oxidative coupling of thiols

At first, catalyst (0.005 g) was added to a mixture of thiol (1 mmol) and H_2O_2 (0.4 mL) in ethanol (2 mL). Then the mixture was stirred for the appropriate time at room temperature. The progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and the mixture was washed with ethyl acetate. Afterward, the products were extracted with ethyl acetate. Then, the solvent of product was removed to give the pure disulfides.

4.8 Selected spectral data

Dibenzyl sulfoxide (Table 3, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 3.90 (d, 2H, J= 12.8 Hz), 3.95 (d, 2H, J= 12.8 Hz), 7.29-7.43 (m, 10H) ppm.

Dodecyl methyl sulfoxide (Table 3, entry 10). ^{1}H NMR (400 MHz, DMSO): δ_H= 0.87 (t, *J*=6.8, 3H), 1.26–1.71 (m, 20H), 2.58(s, 3H), 3.09 (t, *J*=8, 2H) ppm.

1,2-Bis(4-bromophenyl)disulfane (Table 5, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.44 (t, *J* = 8, Hz, 4H), 7.53 (t, *J* = 8, Hz,4H) ppm.

1,2-Di(naphthalen-2-yl)disulfane (Table 5, entry 11). ^{1}H NMR (400 MHz, DMSO): δ_H= 7.50–7.57 (m, 4H), 7.67–7.75 (m, 2H), 7.89–7.93 (m, 4H), 7.96-8.00 (m, 2H), 8 (s, 2H) ppm.

1,2-Bis(4,6-dimethylpyrimidin-2-yl)disulfane (Table 5, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H= 2.50 (s, 12H), 6.87 (s, 2H) ppm.

Acknowledgements

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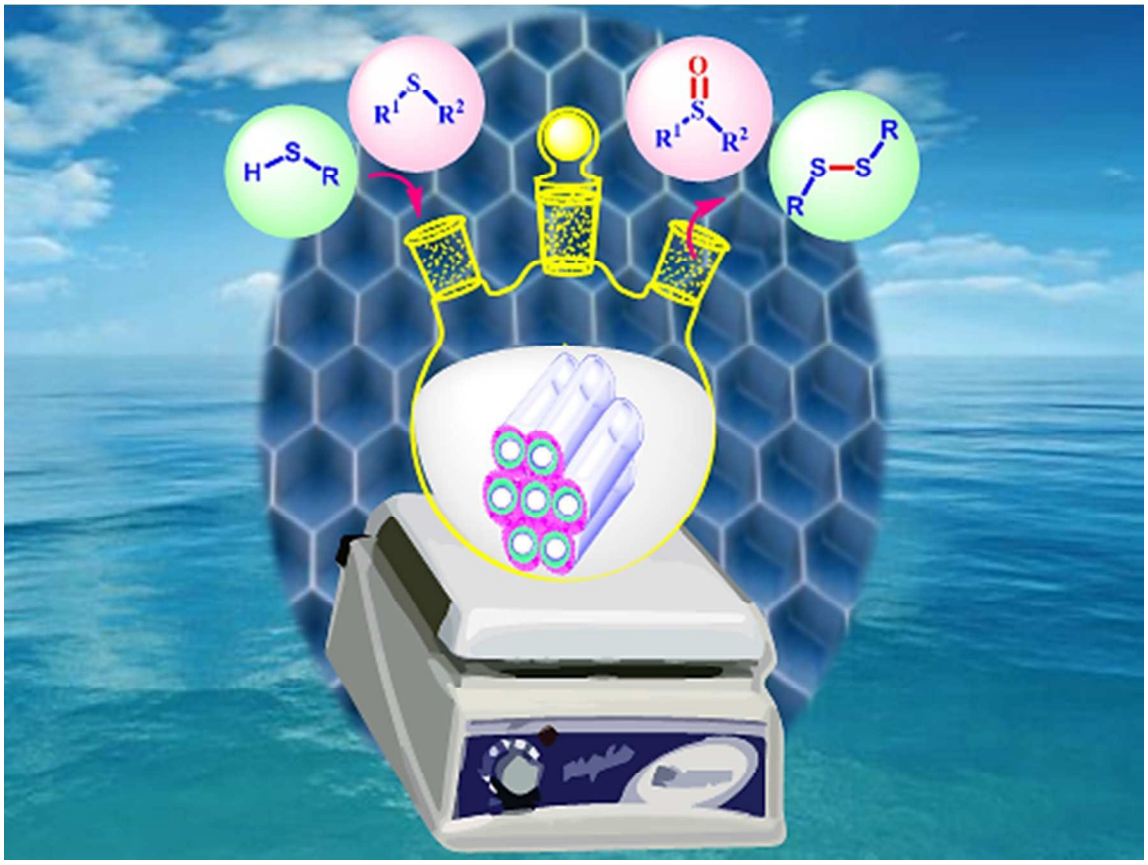
Graphical abstract

A highly efficient, green, rapid, and chemoselective oxidation of sulfur containing compounds in presence of MCM-41@creatinine@M (M= La and Pr) mesostructured catalyst under neat conditions

Taiebeh Tamoradi,[a] Mohammad Ghadermazi,[a,*] Arash Ghorbani-Choghamarani [b,*]



MCM-41@creatinnine@M (M= La and Pr) as highly efficient and reusable heterogeneous catalyst prepared by a simple procedure for the oxidation of sulfur containing compounds.

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