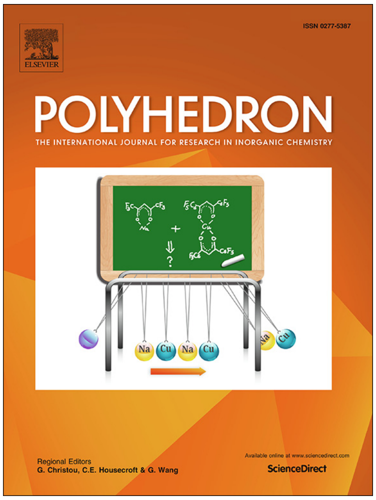

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# Anchoring Mn(IV) in multi pyridine modified mesoporous silica SBA-15 : An efficient nanocatalyst for selective oxidation of sulfides to sulfoxides

Saba Hemmati,*[,a] Malak Hekmati,[b] Delafarin Salamat,[c] Mohammad Yousefi,*[,d] Bikash Karmakar,*[,e] Hojat Veisi[a]

[a]Department of Chemistry, Payame Noor University, Tehran, Iran
[b]Department of Organic Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran
[c]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[d]Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran
[e]Department of Chemistry, Gobardanga Hindu College, 24-Parganas (North), India

E-mails: s_organo2007@yahoo.com (S. Hemmati), myousefi50@hotmail.com (M. Yousefi), bikashkarm@gmail.com (B. Karmakar)

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## Abstract

In this current study we report the implementation of Mn(IV) grafted multipyridine linked melanine functionalized SBA-15/CCPy/Mn(OAc)$_2$ as a novel high surface area nanocatalyst. The melamine linked multipyridine ligand was introduced over mesoporous SBA-15 to ensure the strong chelation of Mn(OAc)$_2$ in order to deploy as active site. The structural features of the so designed material were properly analyzed with SEM, TEM, EDX, ICP-AES and $N_2$ adsorption-desorption isotherm techniques. Catalytic behavior of the nanocomposite was investigated in the chemoselective oxidation of sulfides to sulfoxides using $H_2O_2$ as a mild oxidant under solvent-free conditions at room temperature resulting very good yields. The catalyst was reused up to 8 consecutive cycles without significant leaching and reduced catalytic performance.

**Keywords:** Mesoporous, poly-ligand, Mn(IV), Hydrogen peroxide, oxidation, Sulfides, Sulfoxides, reusable

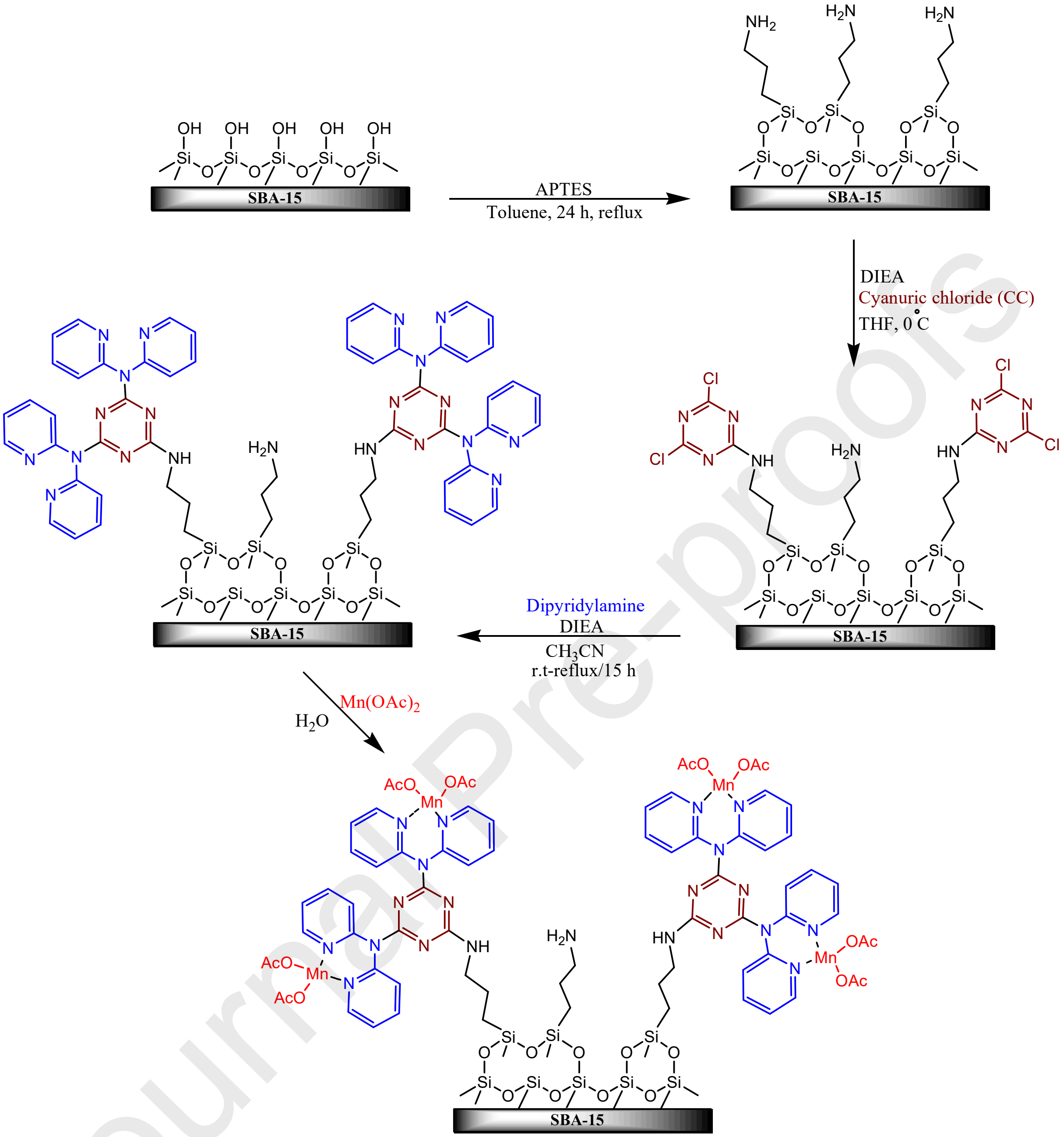
## 1. Introduction

The metal ion-Schiff base complexes have been of special interest in academia and industries due to their profuse applications in different arena like catalysis, biomedical investigations and electrochemistry [1-4]. Among different metals, the transition metals acquire great affinity to form broad range of complexes with different kinds of organic ligands. Especially, their Schiff base complexes have been largely applied as effective homogeneous catalysts. Nevertheless, the issues of catalyst isolation, regeneration and reusability have been the major drawbacks during the reactions [5-12]. Thereby, heterogenization of those catalysts by immobilizing over different solid supports like organosilicon compounds [13,14], $Fe_3O_4$ nanoparticles [15], carbon nanotubes [16], mesoporous silica [17,18], zeolites [19,20] and layered materials [21] has been a significant area of concern. In other words, technically, the surface engineering on solid supports by covalent bonding of active catalytic sites has come into prominence to design a quasi-heterogeneous catalytic system in order to adopt several advantages like introducing milder environments, evading the direct contact of hazardous substances and easy recovery and reuse of catalyst following green chemistry standards [22-26].

Now, among various solid heterogeneous supports [27-30], the ordered mesoporous silica (OMS) matrixes acquire special priority. In the last few decades, the catalysis fraternity has extensively accepted SBA-15 as heterogeneous support because of its highly ordered hexagonal honeycomb like morphology with horizontally packed arrays, significantly high surface area, large pore sizes appropriate for organic molecules to fit in, high thermal stability and rigid configuration [31-34]. Moreover, the external surface hydroxyl groups of SBA-15 could be utilized for surface functionalization.

As part of our ongoing research works based on the development of novel heterogeneous catalysts [35], we exploited herein the multipyridine linked melamine organo-moiety as ligand to form covalent bonding with the mesoporous silica surface and thereafter effectively chelated the $Mn(OAc)_2$ salt as a secondary shell. Such surface modifications decrease the affinity of active sites to agglomerate and thereby make them significantly stable, prevent their oxidation and decrease solubility in organic solvents [36, 37]. Subsequently, we investigated the catalytic performance of the so developed material in the chemo-selective oxidation of sulfides to sulfoxides using $H_2O_2$ as a green oxidant.

In recent years sulphoxide chemistry has got tremendous impetus. Organic sulfoxides are found important as chemical intermediates, in medicinal biology as cardiotonic agents, anti-hypertensive, vasodilators, antibacterial, antifungal and anti-atherosclerotics [38-41]. In this current study, we report the chemoselective synthesis of organic sulphoxides catalyzed over Mn(IV) catalyst anchored with multi-pyridine linked melanine functionalized mesoporous silica SBA-15 [SBA-15/CCPy/$Mn(OAc)_2$] (Scheme 1). Heterogeneity of the novel material was investigated via leaching test. It was reused for several times as well with minimal change in its catalytic activity.



**Scheme 1.** Preparation of SBA-15/CCPy/Mn(OAc)$_2$.

## 2. Experimental

### 2.1 Materials and methods

All commercially available chemicals required for the preparation of catalyst were purchased from Aldrich and Fluka. For organic synthesis the corresponding chemicals and different solvents were bought from Merck. All of them were used as such without further purification. Morphology of the mesostructured material were determined by SEM technique using FESEM-TESCAN MIRA3. TEM analysis was carried out with a Philips CM10 microscope operating at 200 Kv. The elemental analysis of the samples was done by Energy dispersive X−ray spectroscopy (EDAX, TSCAN).

### 2.2 Synthesis of functionalized organo-functionalized SBA-15

The mesoporous silica SBA-15 was synthesized according to our previously reported method [42]. 3.0 g SBA-15 was suspended in 30 mL anhydrous toluene under stirring in a 100 round bottomed flask. For amino functionalization 1.5 mmol of aminopropyl triethoxy silane (APTES) was then added to it dropwise and the mixture was refluxed for 24 h at $N_2$ atmosphere. It was then filtered and washed successively with toluene, dichloromethane and methanol. The aminopropyl derivative of SBA-15 was obtained as a white powder after drying under vacuum at 80 $^{o}$C for 10 h. Subsequently, 3.0 g of the initial derivative was suspended in 35 mL tetrahydrofuran (THF) and then 0.5 mL diisopropyl ethylamine (DIPEA) was added. A 5 mL THF solution of cyanuric chloride (CC) was added to the mixture at 0 $^{o}$C and then stirred at room temperature for another 2 h. Then the solution was decanted and the residue was washed with 50 mL THF. Without isolation, the material was again suspended in 25 mL acetonitrile and 1.0 mL DIPEA was added at room temperature. 1.2 g of dipyridylamine (Py) (7.0 mmol) was further added at room temperature and the mixture was refluxed for 15 h. Finally, the resulting solid was filtered, washed with DI water followed by acetone. Thereby, the SBA-15/CCPy nanocomposite was obtained after drying at 50 $^{o}$C for 12 h.

### 2.3 Synthesis of $Mn(OAc)_2$ immobilized SBA-15/CCPy [SBA-15/CCPy/Mn(IV)]

For the Mn anchoring procedure, 1.0 g of SBA-15/CCPy was suspended in 50 mL deionized water via sonication. A 10 mL aqueous solution containing 0.17 g of $Mn(OAc)_2$ salt (1.0 mmol) was added slowly to the suspension and the mixture was stirred at 25 °C for 24 h. The solid product was isolated by filtration and washed several times with water and ethanol successively. Finally the nanocomposite was dried under vacuum at 100 ˚C for 24 h to have SBA-15/CCPy/$Mn(OAc)_2$. Elemental analysis of the material via ICP-AES technique revealed 0.71 mmol/g loading of Mn.

### 2.4. General procedure to synthesize sulfoxides

To 1.0 mmol organic sulfide 1.5 mmol 30% (w/w) $H_2O_2$ was added at solvent-free condition in presence of 15 mg SBA-15/CCPy/$Mn(OAc)_2$ (1 mol%) catalyst. The mixture was stirred for requisite time at ambient temperature. Progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the catalyst was isolated from the mixture by filtration and the products were extracted with $Et_2O$ and concentrated to afford the pure products.

## 3. Results and discussion

The novel material SBA-15/CCPy/$Mn(OAc)_2$ was synthesized through post-functionalization over the high surface matrix. The structural morphology and physicochemical behaviors of the material were investigated through different analytical techniques like Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDX), ICP-AES and BET surface area analysis. The SEM image demonstrates a rod-shaped morphology being aggregated into bundles (Fig. 1a). The small dots distributed over the surface are indication of possible surface modifications and metal doping. A better structural insight can be observed from TEM images. The three dimensional parallel channel of hexagonal pores, characteristic of SBA-15, are clearly visible from Fig. 1b. The dark shades over the surface are possibly due to the surface modifications and Mn insertion. It clearly reveals that functionalization over SBA-15 did not affect the basic morphology of the material.

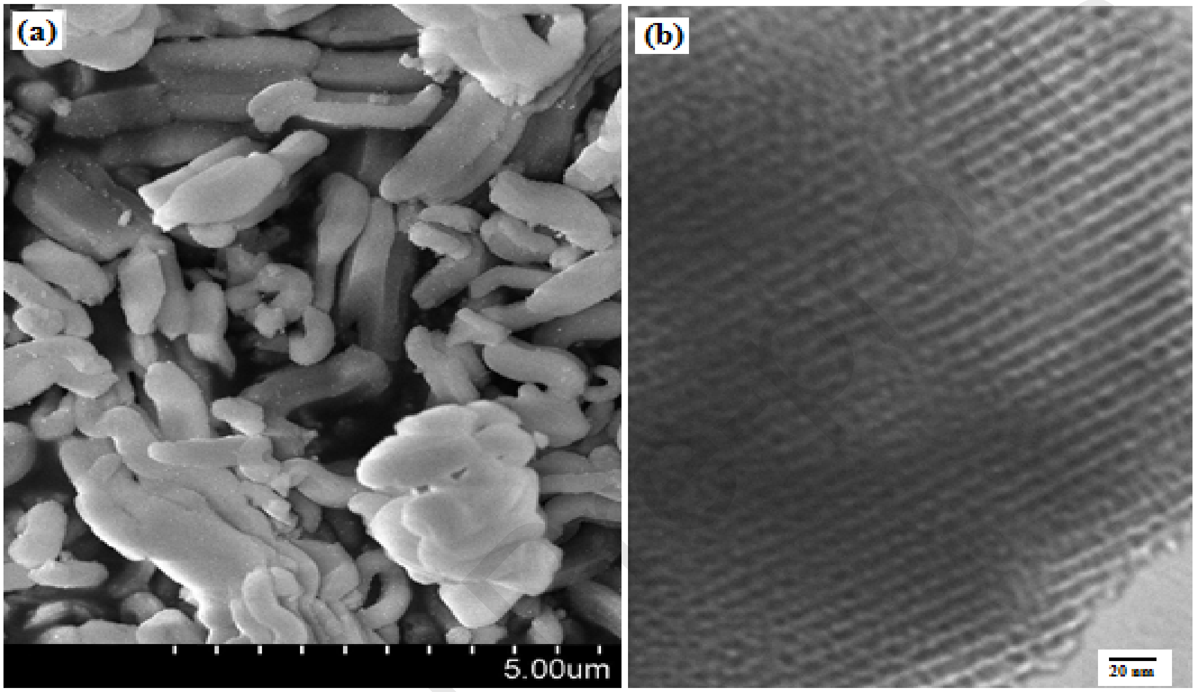


**Fig. 1.** a) SEM and b) TEM images of SBA-15/CCPy/Mn(OAc)$_2$.

The EDX analysis confirms the presence of N, O, C, Si and Mn as elements present in the prepared material (Fig. 2). N, O and C elements justifies the surface functionalization over the Si surface.

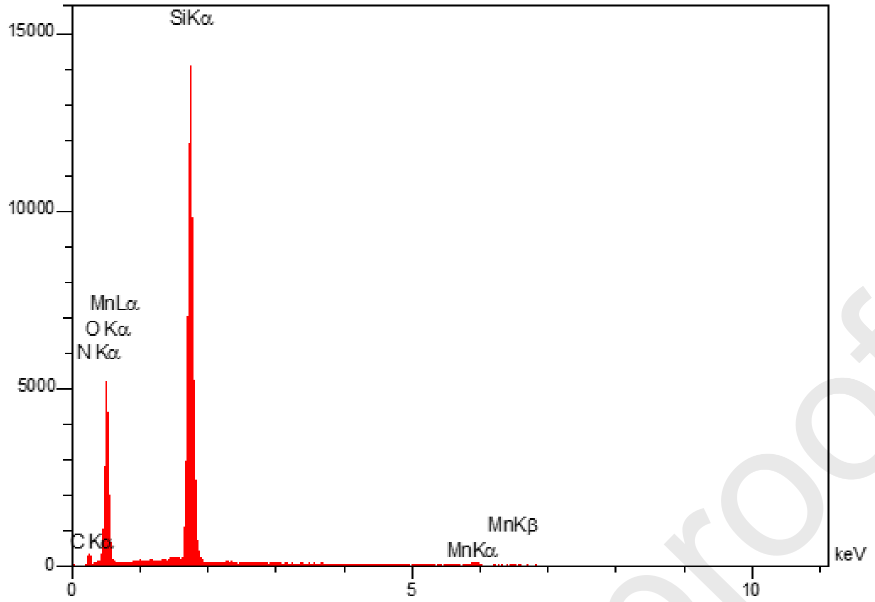


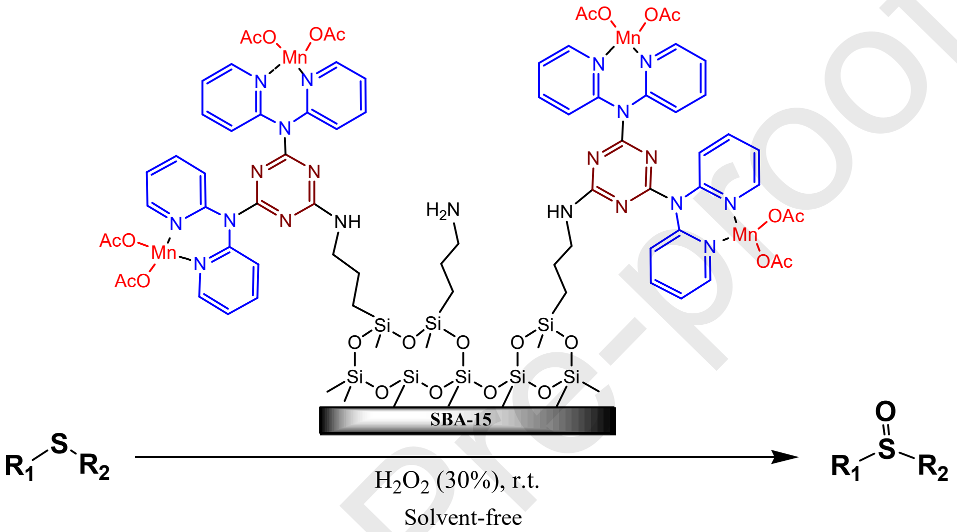
**Fig. 2.** EDX analysis of SBA-15/CCPy/Mn(OAc)$_2$ nanocomoposite.

While dealing with mesoporous materials surface analysis is essential criteria. Thereby, nitrogen gas adsorption-desorption isotherm analysis was performed for the SBA-15/CCPy/Mn(OAc)$_2$ material and the corresponding data have been depicted in Table 1. The bare SBA-15 matrix exerts an ample surface area of 752 m$^2$/g as determined by BET method. However, due to surface loading it was enormously reduced to 371 m$^2$/g. The pore volume and mean pore diameter also were decreased because of the modification.

**Table 1.** The structure parameters of SBA-15 and SBA-15/CCPy/Mn(OAc)$_2$

| **Entry** | **Samples** | **S$_{BET}$ (m$^2$g$^{-1}$)** | **Total pore volume (cm$^3$g$^{-1}$)** | **Mean pore diameter (nm)** |
|---|---|---|---|---|
| 1 | SBA-15 | 752 | 0.810 | 7.02 |
| 2 | SBA-15/ CCPy/Mn(OAc)$_2$ | 371 | 0.619 | 4.62 |

After the meticulous structural analysis, it was the turn of investigating catalytic performance of SBA-15/CCPy/Mn(OAc)$_2$ which was done in the selective oxidation of organic sulphides. In view of maintaining green chemistry criteria we used 30% $H_2O_2$ as non-hazardous oxidant and carried out the reactions at room temperature under solvent-free conditions (Scheme 2).



**Scheme 2.** Catalytic application of SBA-15/CCPy/Mn(OAc)$_2$ towards the synthesis of sulfoxides from sulfides using $H_2O_2$.

However, prior to any generalized reaction protocol, it was obligatory to investigate the best possible conditions and thereby the oxidation of methyl phenyl sulfide was selected as a reference reaction. Different reaction parameters like catalyst mol%, $H_2O_2$ mol% and solvent were imposed thereupon. The results have been documented in Table 2. The reaction was not much successful in the absence of SBA-15/CCPy/Mn(OAc)$_2$ catalyst even after a prolonged run (Table 2, entries 1-2) ensuring the active role of Mn. 1 mol% Mn loaded catalyst was found to be optimum among different concentrations (Table 2, entries 3-6). Again, keeping the best catalyst a screening of solvent was carried out and among them solvent-free condition resulted the best (Table 2, entries

8-11). Ultimately, 1 mol% catalyst (15 mg), 2.0 mmol $H_2O_2$ and solvent-free conditions at room temperature were chosen as optimum conditions to convert methyl phenyl sulfide to corresponding sulfoxide with excellent yields (Table 2, entry 5).

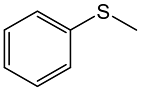
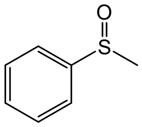
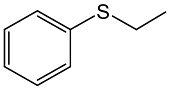
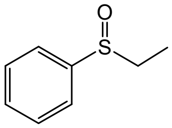
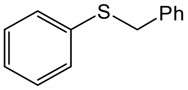
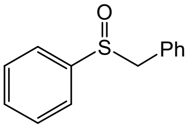
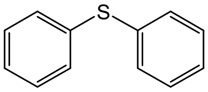
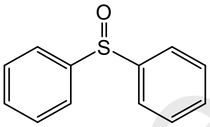
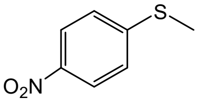
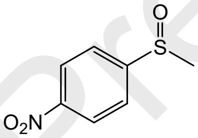
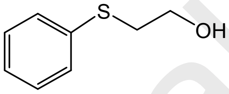
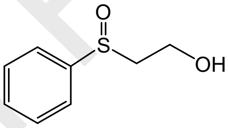
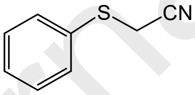
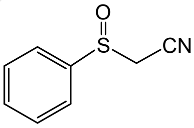
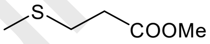
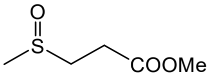
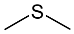
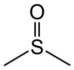
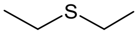
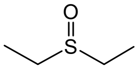
**Table 2.** Optimization of conditions for the conversion of methyl phenyl sulfide to methyl phenyl sulfoxide over SBA-15/CCPy/$Mn(OAc)_2$ and $H_2O_2$

| Entry | Catalyst (mol%) | $H_2O_2$ (mmol) | Solvent | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | Catalyst-free | 2.0 | Solvent-free | 12 h | 35 |
| 2 | SBA-15/CCPy (10) | 2.0 | Solvent-free | 12 h | 40 |
| 3 | SBA-15/CCPy/$Mn(OAc)_2$ (0.25) | 2.0 | Solvent-free | 2 h | 95 |
| 4 | SBA-15/CCPy/$Mn(OAc)_2$ (0.50) | 2.0 | Solvent-free | 45 | 95 |
| 5 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 2.0 | Solvent-free | 10 | 95 |
| 6 | SBA-15/CCPy/$Mn(OAc)_2$ (1.25) | 2.0 | Solvent-free | 10 | 95 |
| 7 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 1.0 | Solvent-free | 45 | 88 |
| 8 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 3.0 | Solvent-free | 10 | 80 |
| 9 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 2.0 | EtOH | 45 | 95 |
| 10 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 2.0 | $CH_3CN$ | 45 | 95 |
| 11 | SBA-15/CCPy/$Mn(OAc)_2$ (1.00) | 2.0 | $CH_2Cl_2$ | 3 h | 85 |

[a] Determined by GC.

After settling the optimum conditions, the scope and generality of the recommended approach as an easy and effective technique for the oxidation of aliphatic and aromatic sulfides was studied and the results are shown in Table 3. A wide variety of aliphatic and aromatic sulphides are well compatible under the protocol affording good to excellent yields. The sulfides with sensitive functional groups (OH, CN and COOMe) could be oxidized with tremendous chemo-selectively (Table 3, entries 6-8). The turnover frequencies (TOF) and turnover numbers (TON) in all the cases were found to be outstanding at very short reaction times.

**Table 3.** Selective oxidation of sulfides to sulfoxides in the presence of SBA-15/CCPy/Mn(OAc)$_2$ under optimized conditions.[a]

| Entry | Sulfide | Sulfoxide | Time (min) | Yield (%)[b] | TOF (h$^{-1}$)[c] | TON (h$^{-1}$)[d] |
|---|---|---|---|---|---|---|
| 1 |  |  | 10 | 95 | 570 | 95 |
| 2 |  |  | 10 | 95 | 570 | 95 |
| 3 |  |  | 10 | 96 | 576 | 96 |
| 4 |  |  | 15 | 85 | 340 | 85 |
| 5 |  |  | 15 | 90 | 360 | 90 |
| 6 |  |  | 8 | 95 | 712.5 | 90 |
| 7 |  |  | 10 | 88 | 528 | 88 |
| 8 |  |  | 12 | 75 | 375 | 75 |
| 8 |  |  | 12 | 85 | 425 | 85 |
| 10 |  |  | 12 | 88 | 440 | 88 |

[a]Reaction conditions: sulfide (1 mmol), 30% $H_2O_2$ (2.0 mmol), SBA-15/CCPy/Mn(OAc)$_2$(15 mg, 1.0 mol%), rt.
[b]Isolated yield.
[c]TOF = (Yield/Time)/Amount of catalyst (mol).
[d]TON = Yield/Amount of catalyst (mol).

In order to explore the reusability of SBA-15/CCPy/Mn(OAc)$_2$, the catalyst was taken out of the reaction mixture after completion, regenerated after drying and applied once again for the next run. To our anticipation, the catalyst could be used up to 8 successive runs in oxidizing methyl phenyl sulfide to the its sulfoxide (Fig. 3). After the successful 7 runs, the catalyst was carefully filtered out of the reaction mixture and leaching of Mn into the solution was evaluated by ICP-AES check which resulted only a 1.12%, showing the robustness of catalyst.

**Fig. 3.** Reusability of SBA-15/CCPy/Mn(OAc)$_2$ nanocatalyst.

To determine the heterogeneity of the catalyst, a hot filtration test was conducted for the same reaction under the optimized conditions. After a half time of the reaction, the catalyst was isolated from the reaction mixture by filtration and the reaction was allowed to continue. There was no further increase in the yield, verifying the heterogeneity of the catalyst.

The viability of our protocol in the oxidation of sulfides was further justified by comparison with literature reports. As shown in Table 4, the previously reported procedures suffer from several drawbacks like longer reaction times, use of costlier transition metals, need of volatile and/or toxic organic solvents and much lower TOF. Evidently, our method is superior to them in overcoming all the said drawbacks which ascertains the efficiency of SBA-15/CCPy/Mn(OAc)$_2$ catalyst for selective sulfide oxidations.

**Table 4.** Comparison of our work with reported procedures in the synthesis of methyl phenyl sulfuxide.

| Entry | Reaction conditions | Time (min) | Yield % | TOF ($h^{-1}$) | Ref. |
|---|---|---|---|---|---|
| 1 | SBA-15/CCPy/Mn(OAc)$_2$, solvent-free, R.T. | 10 | 95 | 570 | This work |
| 2 | MNPs-Pr-NHSO$_3$H, solvent-free, R.T. | 80 | 100 | 78.9 | [43] |
| 3 | MCM-Mo, $CH_3CN$, 40 ºC | 60 | 99 | 839 | [44] |
| 4 | SiO$_2$-based tungstate interphase, $CH_3OH/CH_2Cl_2$, R.T. | 90 | 82 | 27.3 | [45] |
| 5 | Peroxotungstate/SiO$_2$, $CH_3OH/CH_2Cl_2$, 8 ºC | 150 | 92 | 24.5 | [46] |
| 6 | VO(acac)$_2$/Resin, $H_2O$, R.T. | 10 | 98 | 98 | [47] |
| 7 | $Fe_3O_4$@SiO$_2$/Mo, $CH_3CN$, 50 ºC | 90 | 92 | 20.4 | [48] |
| 8 | VO(IV)–MCM-41, EtOH, R.T. | 480 | 95 | -$^c$ | [49] |
| 9 | VO(IV) Schiff base complexes, EtOH, R.T. | 10 | 100$^a$ | -$^c$ | [50] |
| 10 | VO(IV) Schiff base complex, solvent-free,45 °C | 50 | -$^b$ | -$^c$ | [51] |

[a] Conversion (%).
[b] The major product is sulfone.
[c] The catalyst's mol% is not reported.

## 4. Conclusion

In conclusion, we have developed a post grafting approach to synthesize the novel Mesoporous nanocatalyst of Mn(OAc)$_2$ immobilized on multipyridine linked melamine modified SBA-15, i.e. SBA-15/CCPy/Mn(OAc)$_2$. We applied the material in the selective oxidation of various sulfides to their mono-sulfoxides using $H_2O_2$ as green oxidant at room temperature under solvent-free conditions. All the products were obtained in high yield with excellent TOF. The catalyst was sufficiently stable as it could be reused as much as eight times. There was negligible amount of leaching of active species into the reaction mixture as well, as confirmed from ICP-AES studies. A comparison study with the reported procedures also justified the uniqueness of this protocol.

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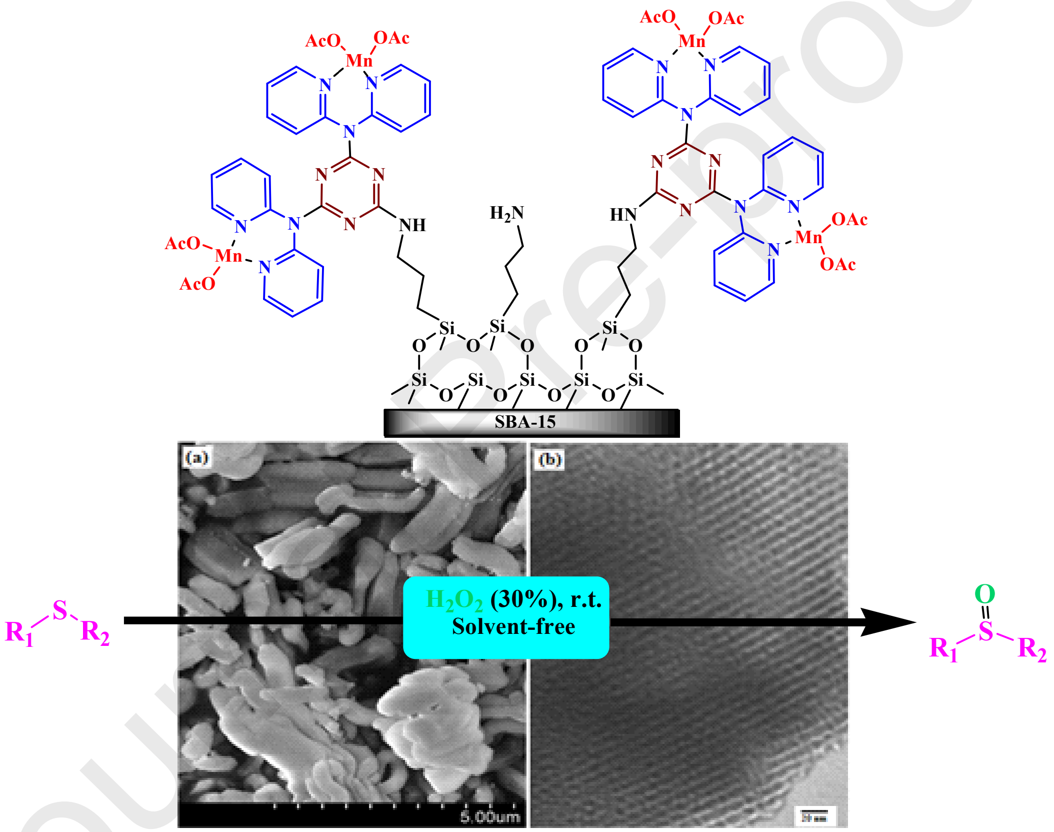
## Graphical Abstract

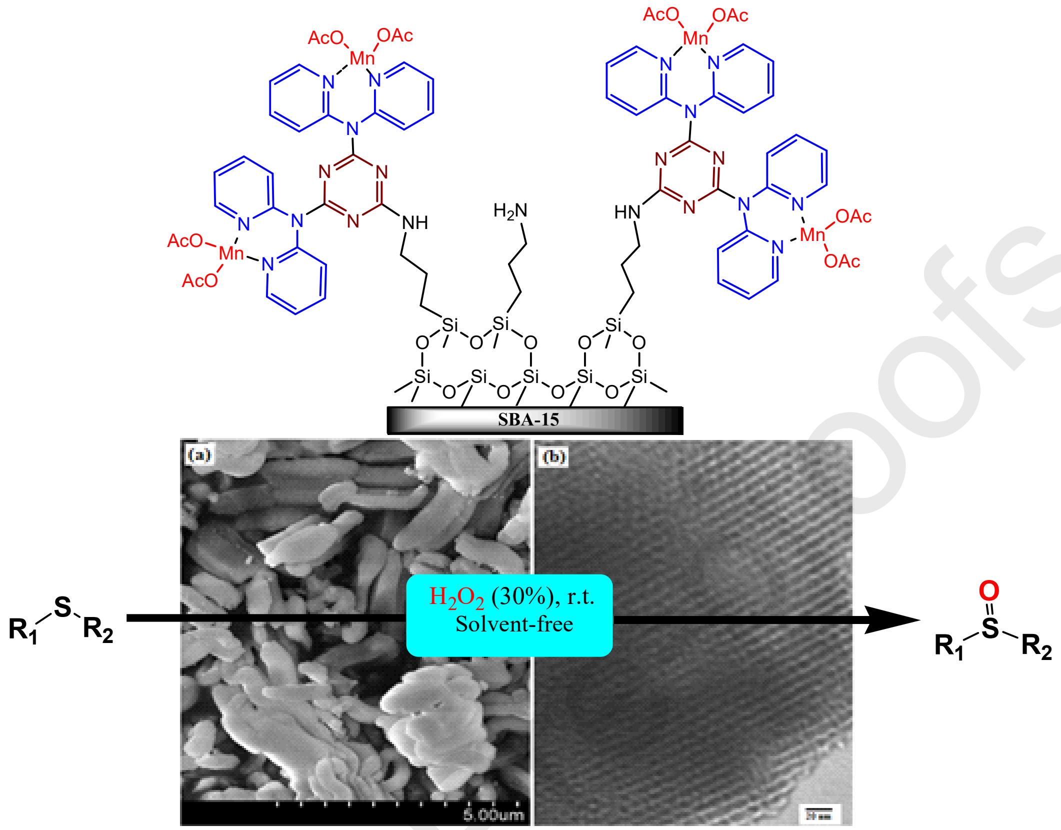
# Anchoring Mn(IV) in multi pyridine modified mesoporous silica SBA-15: An efficient nanocatalyst for selective oxidation of sulfides to sulfoxides

Saba Hemmati,*Malak Hekmati, Delafarin Salamat, Mohammad Yousefi,*Bikash Karmakar,*
Hojat Veisi*



### Conflict of Interest

The authors report no conflicts of interest in this work.



## Graphical Abstract

# Anchoring Mn(IV) in multi pyridine modified mesoporous silica SBA-15: An efficient nanocatalyst for selective oxidation of sulfides to sulfoxides

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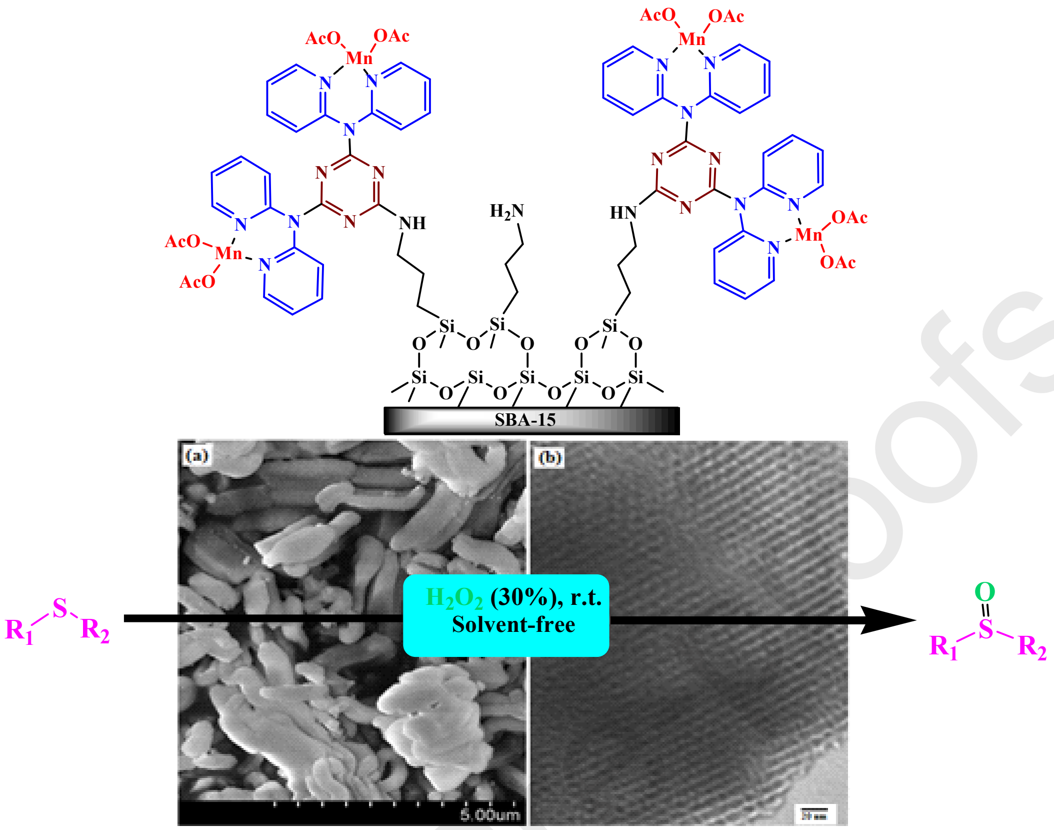

Dear Editor

Please attached find a copy of the manuscript entitled “*Anchoring Mn(IV) in multi pyridine modified mesoporous silica SBA-15: An efficient nanocatalyst for selective oxidation of sulfides to sulfoxides”* which I would like you to consider it to be published in the ***Polyhedron.***

Due to the aforementioned motives and also as a component of our enduring research program on the utilization of catalysts for the development of beneficial new synthetic methodologies [36], we reporting on the technique implemented in SBA-15/CCPy/Mn(OAc)2 preparation as a novel Mesoporous nanocatalyst, while melamine bearing pyridine groups on SBA-15 were applied for securing Mn(OAc)2 catalyst as capping agent. TEM, SEM, ICP, BET, and EDX analysis were done to specify the resultant catalyst. The chemoselective oxidation of sulfides was catalyzed by SBA-15/CCPy/Mn(OAc)2 to sulfoxides with hydrogen peroxide as a green oxidant in high yields at room temperature. The catalyst was recycled up to 7 times with no significant leaching and reduced catalytic activity.We believe that this paper is well-suited for publication in the ***Polyhedron.***

I have to add that this submission is original and all co-authors are aware of the submission and agree to its publication in the Journal. This work is novel/original and is not under consideration for publication elsewhere.

Thank you, in anticipation, for your consideration of this matter.

With the sincere regards

Hojat Veisi,

Associat. Prof. of Org. Chem.
Department of Chemistry, Payame Noor University (PNU), Iran
E-mail: ***hojatveisi@yahoo.com***