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Research paper

Nanoarchitecturing of open metal site Cr-MOFs for oxodiperoxo molybdenum complexes [$MoO(O_2)_2$@En/MIL-100(Cr)] as promising and bifunctional catalyst for selective thioether oxidation

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ABSTRACT

In this work, open metal site metal-organic framework of MIL-100(Cr) was selected as a support for the multi-step grafting of molybdenum complexes. The oxodiperoxo molybdenum complexes were coordinated onto the ethylene diamine-decorated MIL-100(Cr) pore cage, that this bifunctional $MoO(O_2)_2$@En/MIL-100(Cr) catalyst was successfully applied for H_2O_2 (30%) mediate green and selective thioether oxidation process. Component activity and recyclability test for the $MoO(O_2)_2$@En/MIL-100(Cr) catalyst showed a successful reusability for 8 runs.

1. Introduction

Nanoarchitectonics are expected to achieve an effective guidance in fabricating functional nanoporous materials. Nano-orientation of materials is a widely demanding tool in nanoarchitecturing to reach out a new material with higher surface area [1–4]. Among them, creating an organic-inorganic hybrid nanoporous metal-organic frameworks (MOFs) material is one of the important and crucial parts of research areas [1,5–8].

Nanoporous organic-inorganic hybrid metal-organic frameworks (MOFs) are self-assembled from organic linkers and inorganic connectors of metal ions/clusters, that they have interesting perspectives in the application of catalysis as they exhibit chemical/mechanical/physical properties differing from the usual inorganic metal oxides [9–11]. The possible organization of active centers like metallic connectors, linkers, and their chemical synthetic functionalization on the nanoscale shows potential to build up MOFs particularly modified for catalytic challenges [11]. Among them, metal-organic frameworks with open metal sites are promising candidates for gas capture, and recently, metal-grafting to catalysis purposes [8,12,13]. However, for all practical applications, the choice of the MOF and ligand prevent aggregation, leaching of metal and also mass transferring are necessary. Corma and Garcia et al., extensively synthesized various bifunctional M^{n+}/M^{m+}-MOFs with variable catalytically active centers [12,14–17]. Recently, Lu [18], Guan [19], Xu [20], Fischer [21] and others reported transition metal supported MOFs as efficient catalyst in some organic transformations. On the other hand, new type of metal-organic frameworks with open metal sites are promising candidates for gas capture and catalysis [22–25]. Our group [8] and Corma [12] have recently reported on the catalytic application of open metal site metal-organic frameworks featuring directed ligand grafted to metal center of MOFs to leading bifunctional MOFs with various abilities. In the works, we have reported the use of the Cu-BDC and Corma used $Cu_3(BTC)_2$ as an bifunctional open metal site MOF catalyst containing palladium and copper (II) for the Suzuki reaction and annulation of acetylenic compounds, respectively. In other interesting work Abbasi et al. also grafted the molybdenum ions inside pore channels of $Cu_3(BTC)_2$ to achieve Mo-Cu/MOF as good catalyst in epoxidation of alkenes.

It is also of much interest to design stable bifunctional open metal site MOF catalysts with commercially available and cheap ligands and metal. This is not only of interest from the point of view of catalysis, but also decrease investment costs because of process intensification. We have recently reported on the catalytic application of metal-organic frameworks featuring Al^{+3}, Cu^{+2} and Zn_4O ions/clusters coordinated to carboxylates acids [26–29]. However, in spite of the extensive advantages, the use of these MOFs as catalysts is relatively limited with regard to applications for direct metal

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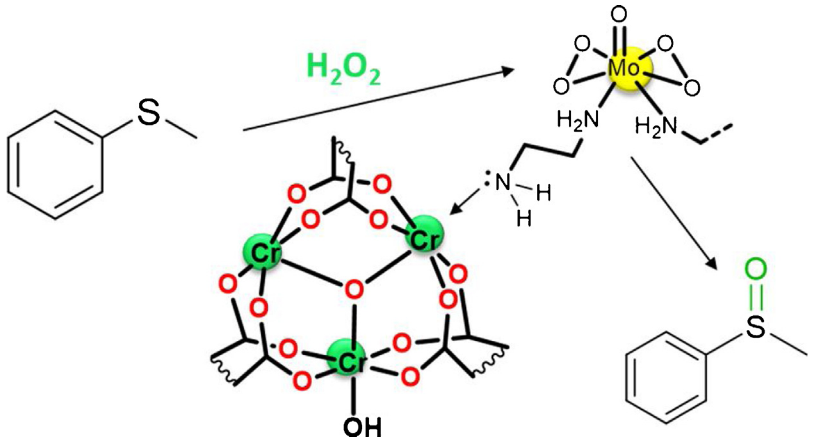


Fig. 1. Bifunctional $MoO(O_2)_2$@En/MIL-100(Cr) for green and selective oxidation of thioether. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

complex grafting. Herein, we have demonstrated chromium benzene tricarboxylate of MIL-100(Cr) as an efficient open metal site Cr-MOFs towards the direct grafting of ethylene diamine (En) and then complexation of that with oxodiperoxo molybdenum complexes ($MoO(O_2)_2 \cdot DMF$) to achieve $MoO(O_2)_2$@En/MIL-100(Cr). The synthesized bifunctional Mo/Cr-MOF was then applied as heterogeneous catalyst for H_2O_2 mediated selective thioether oxidation (Fig. 1.).

2. Results and discussion

For aiming a heterogeneous system, oxodiperoxo complexes of Mo have mainly been immobilized on Cr-MOFs (Mo/Cr-MIL-100). Abbasi et al., synthesized a polyoxotungstate into ionic liquid modified MIL-100(Fe) W/Fe-MOF, which was successfully applied to oxidation of alcohols [30]. Roch-Marchal and Horcajada's group prepared a benzene tricarboxylate-based iron MOF molybdenum pre-catalyst of "H_3PMo_{12}@MIL-100(Fe)" with Mo/Fe ratio around 0.95 [31]. As an ongoing research in nanoporous materials [32–34], we herein, synthesized open metal site Cr-MIL-100 using chromium (VI) oxide and 1,3,5-benzene tricarboxylic acid (H_3BTC) as organic linker in hydrothermal conditions for synthesis of MIL-100(Cr). Then, the activated MOF reacted with ethylene diamine (En) moiety to produce free amine grafted MOF (En/MIL-100(Cr)). Afterwards, oxodiperoxo $MoO(O_2)_2 \cdot DMF$ was added to En/MIL-100(Cr) to produce $MoO(O_2)_2$@En/MIL-100(Cr) MOF as a catalyst for further studies (Scheme 1).

FT-IR analyses were obtained for synthesized $MoO(O_2)_2$@En/MIL-100(Cr). Fig. 2 shows the spectra of the starting MIL-100(Cr) compound compared with the samples after oxodiperoxo molybdenum complexes grafting. As for MIL-100(Cr), the band at 2921 cm^{-1} is assigned to aromatic C—H asymmetric stretching vibrations of terephthalic ligands, and the characteristic peak at 1577 and 1453 cm^{-1} are due to C═C vibrations of aromatic ring moiety. The strong peaks at 1644 and 1392 are corresponds to asymmetric and symmetric vibrations of carboxylate anions present in the MOF material[8]. Furthermore, the frequencies of the Cr—O of octahedral CrO_6 of the metal cluster appears at 523 and 668 cm^{-1}. The FTIR of $MoO(O_2)_2$@En/MIL-100(Cr) shows that the structure didn't change considerably after attachment of the Mo onto the surface of the MOF. The appearance of characteristic bands at 937 cm^{-1}, relating to the Mo—O, proves the formation of Mo complexes in the Cr-MOF. Additionally, the existence double bands at 3412 and 3238 cm^{-1}, relating to the —NH_2, proves the ethylene diamine in the MOF structure. It is worth noting that the observed C—N vibration of coordinated ethylene diamine clearly demonstrating the grafting of ethylene diamine ligands onto Cr-CUSs octahedral cluster in the cages of the Cr-MIL-100 and oxodiperoxo molybdenum complexes.

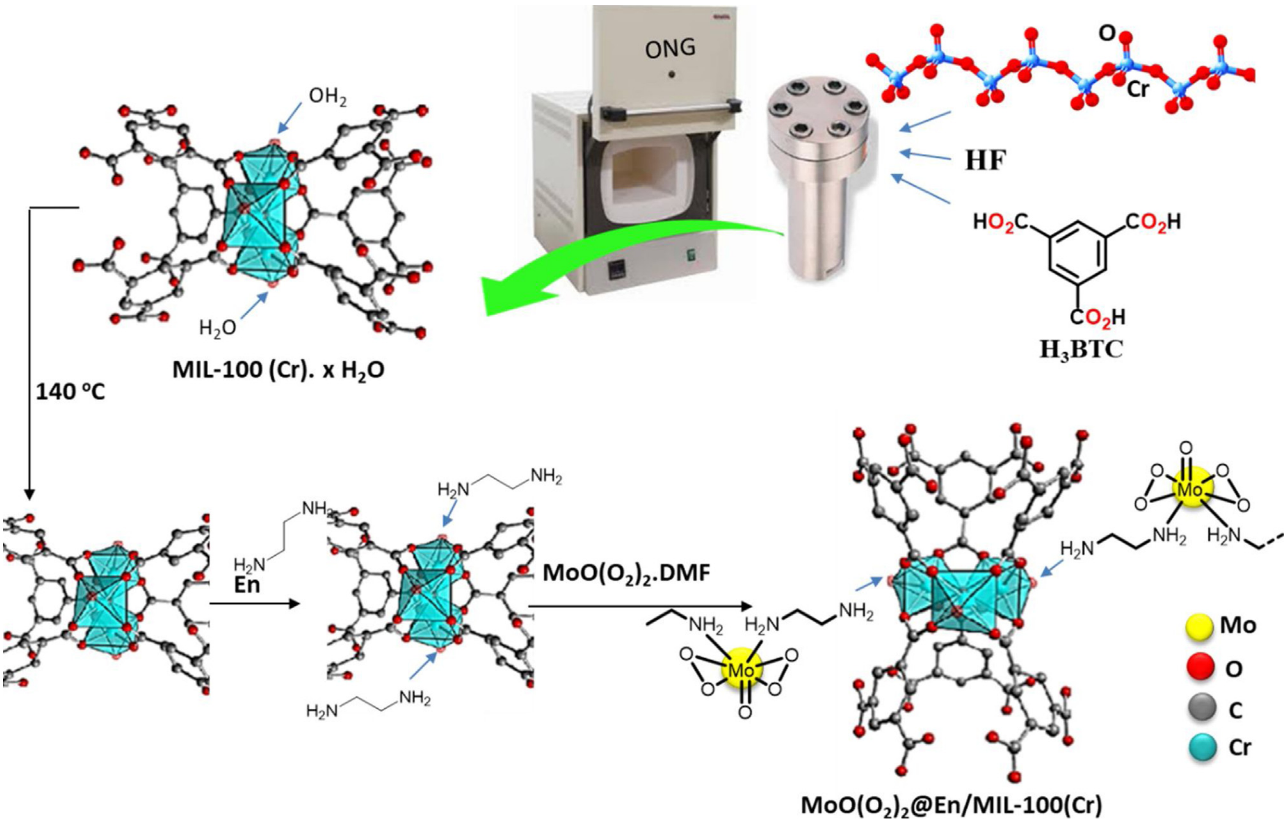
The peaks in the powder diffraction scans were compared against the predicted peaks from the Refs. [35,36]. The XRD patterns of synthesized MIL-100(Cr) in DMF without any activation demonstrate that all the main diffraction peaks (none activated MOF with broad peaks) are in agreement with the predicted pattern (Fig. 3b). Comparison of the predicted XRD patterns of MIL-100(Cr) and the modified sample with the $MoO(O_2)_2 \cdot En$ complex revealed shift for main peak to bigger 2θ angles apart from some slight variations in the Bragg intensities. This behavior represents the expansion of the framework depending on the guest molecules (also higher w% of Mo related to grafted En ligands show that free complex of $MoO(O_2)_2 \cdot DMF$ encapsulated into the MOF pores) inside the pores and clearly confirms the successful grafting (Fig. 3).

To discern the surface morphology of synthesized MIL-100(Cr) and $MoO(O_2)_2$@En/MIL-100(Cr), SEM was carried out. The SEM micrograph of the MIL-100(Cr) revealed the presence of stick sphere MOFs (Fig. 4a). SEM image of $MoO(O_2)_2$@En/MIL-100(Cr) shows its morphology after production (Fig. 4b). In fact, this morphology is similar to morphology of MIL-100(Cr) which indicates that after post-modification and Mo-complexation, the morphology is still intact. Then image profile of the selected area of SEM were measured (Fig. 3c and d). Line profile of the stamper surface of MIL-100(Cr) and $MoO(O_2)_2$@En/MIL-100(Cr) are given in Fig. 4c and d, respectively.

SEM-EDS analysis were performed for the synthesized MOF materials. Based on this analysis, Cr, C, O and N atoms exist in the structure of En/MIL-100(Cr) and Mo, Cr, C, O and N atoms exist in the structure of $MoO(O_2)_2$@En/MIL-100(Cr) which exhibit the successful grafting of Mo to MOF (Fig. 5). To the best of our knowledge, existence of chloride in EDX of $MoO(O_2)_2$@En/MIL-100(Cr) come from the used HCl in preparation of $MoO(O_2)_2 \cdot DMF$ from $NaMoO_4$.

Fig. 6 shows the N_2-adsorption/desorption isotherms of $MoO(O_2)_2$@En/MIL-100(Cr). The MOF isotherm exhibits IV curves with H2-type hysteresis loop and indicates the presence of mesopores. The BET surface area and total pore volume for the prepared $MoO(O_2)_2$@En/MIL-100(Cr) is 219 $m^2 g^{-1}$ and 0.4 $cm^3 g^{-1}$, respectively. The modified sample still possesses a large surface area to provide sufficient space for the introduction of oxodiperoxo molybdenum species.

After sufficient characterization of $MoO(O_2)_2$@En/MIL-100(Cr) and according to industrially interests of oxidation of aromatic thioether [37], it was studied in selective oxidative reaction of thioether using H_2O_2 30%. One of the problems encountered with



Scheme 1. Step-wise synthesis of $MoO(O_2)_2$@En/MIL-100(Cr).

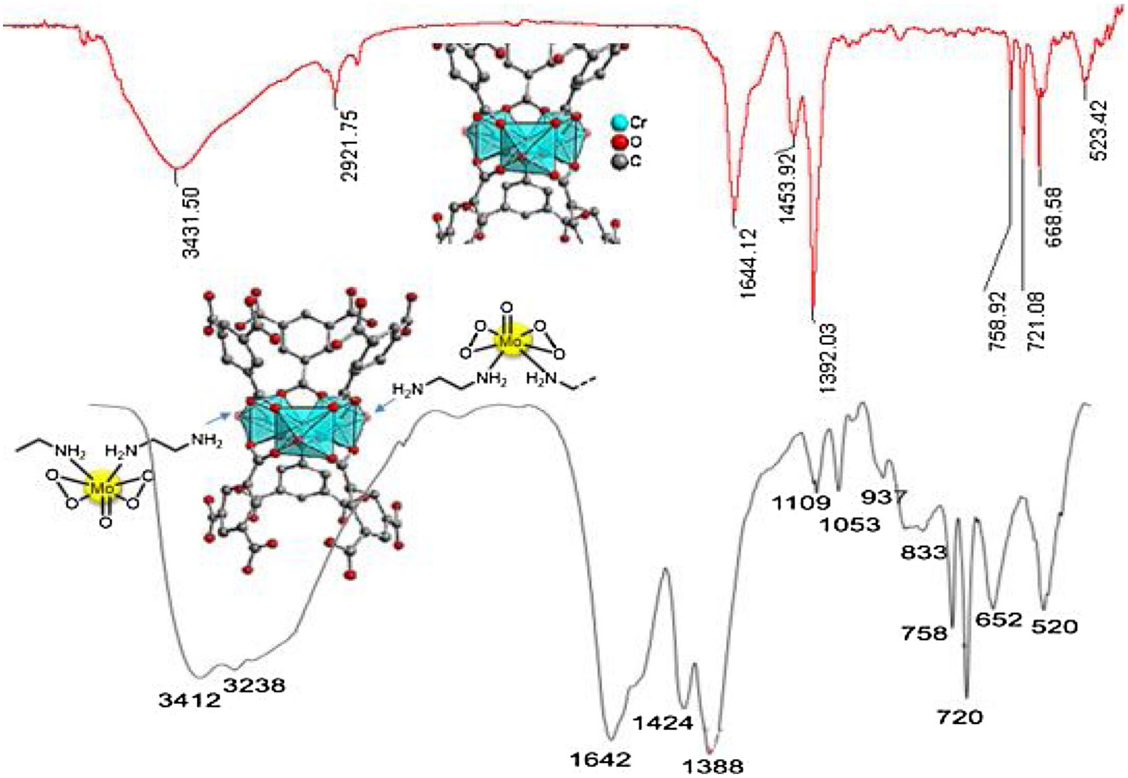


Fig. 2. FT-IR analysis of MIL-100(Cr) and $MoO(O_2)_2$@En/MIL-100(Cr).

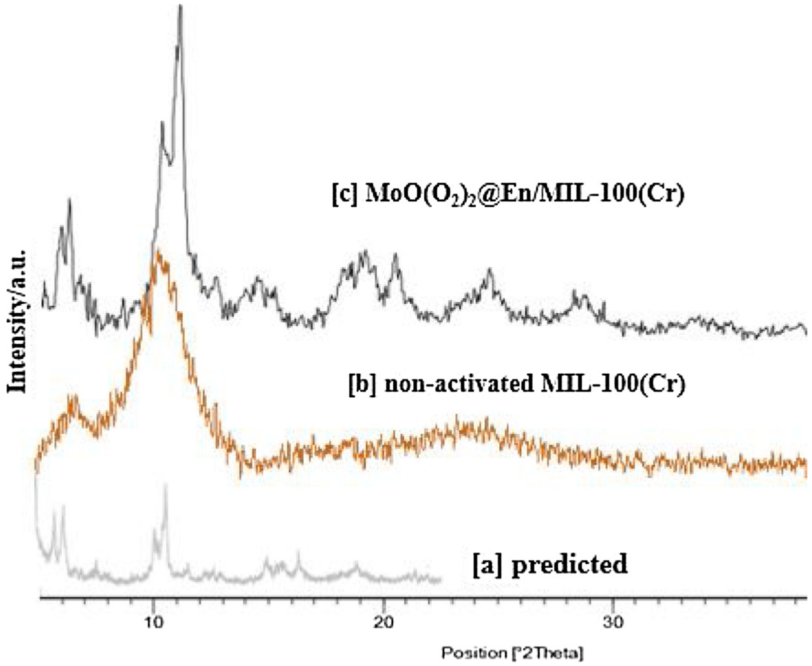


Fig. 3. XRD pattern of (a) predicted, (b) non-activated MIL-100(Cr), and (c) $MoO(O_2)_2$@En/MIL-100(Cr).

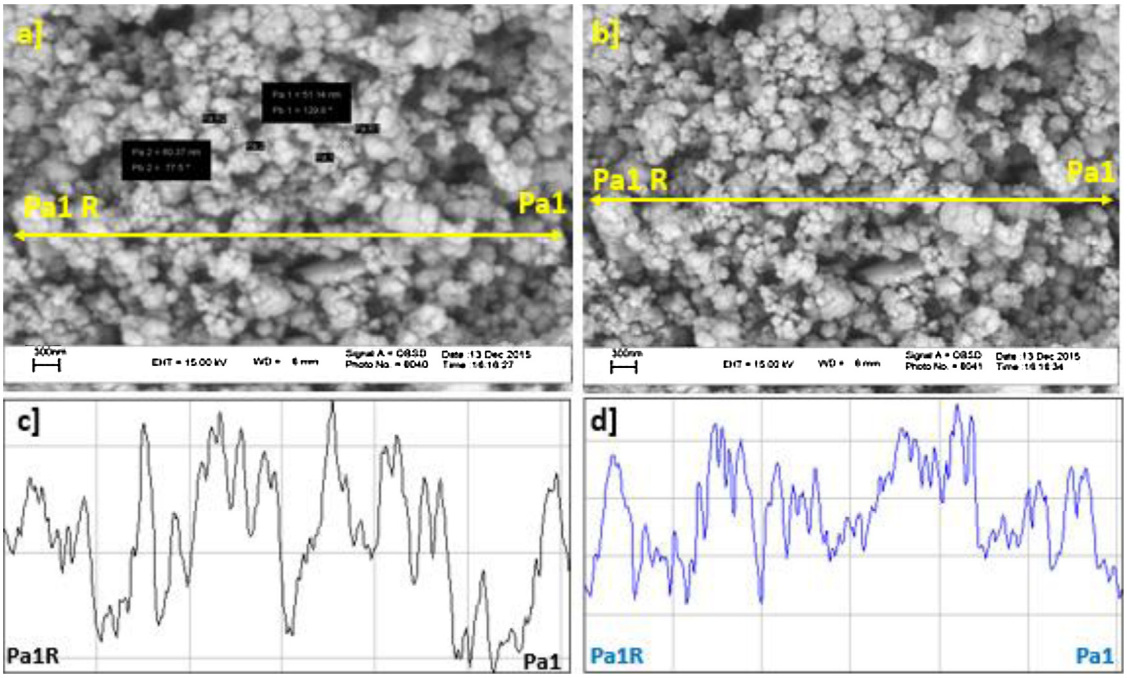


Fig. 4. a) SEM image of a) MIL-100(Cr) and b) $MoO(O_2)_2$@En/MIL-100(Cr). (c, d) Image profile and selected area highlighted of MIL-100(Cr) and $MoO(O_2)_2$@En/MIL-100(Cr).

this method is tramping overoxidation of made thioether oxides to thioether dioxides (sulfones), lacking selectivity and then lead to undesired compounds. In this work, the catalytic ability of the $MoO(O_2)_2$@En/MIL-100(Cr) in the oxidation reaction of thioether without using any salts or stabilization was explored. Oxidation of methyl phenyl sulfide (MPS) as model benchmark reaction was first examined with $MoO(O_2)_2$@En/MIL-100(Cr) using H_2O_2 (Scheme 2).

Various conditions were tested by a model reaction of phenyl methylthioether and under an optimized conditions, $MoO(O_2)_2$@En/MIL-100(Cr) was found to be efficient in the catalysis of green oxidation of phenyl methylthioether. First, the effect of $MoO(O_2)_2$@En/MIL-100(Cr) amount were examined on the model reaction under, including 25 °C, reaction time (30 min), sulfide:H_2O_2 (1:4) and H_2O (1 mL) that reaction scale was 0.5 mmol. Several amounts of catalyst were added to reaction mixtures and among them 0.04 g (18.3 mol% Mo) of supported oxodiperoxo molybdenum complexes was found to be more efficient from the point view of methyl phenyl sulfoxide yield in each reaction (Fig. 7).

Several protic, non-polar and polar solvents were investigated on the selectivity and yield towards sulfoxide product through the model reaction. Among them, H_2O and methanol had better results for selective sulfoxide synthesis. However, due to the fact that water is a nontoxic, available and therefore a greener solvent

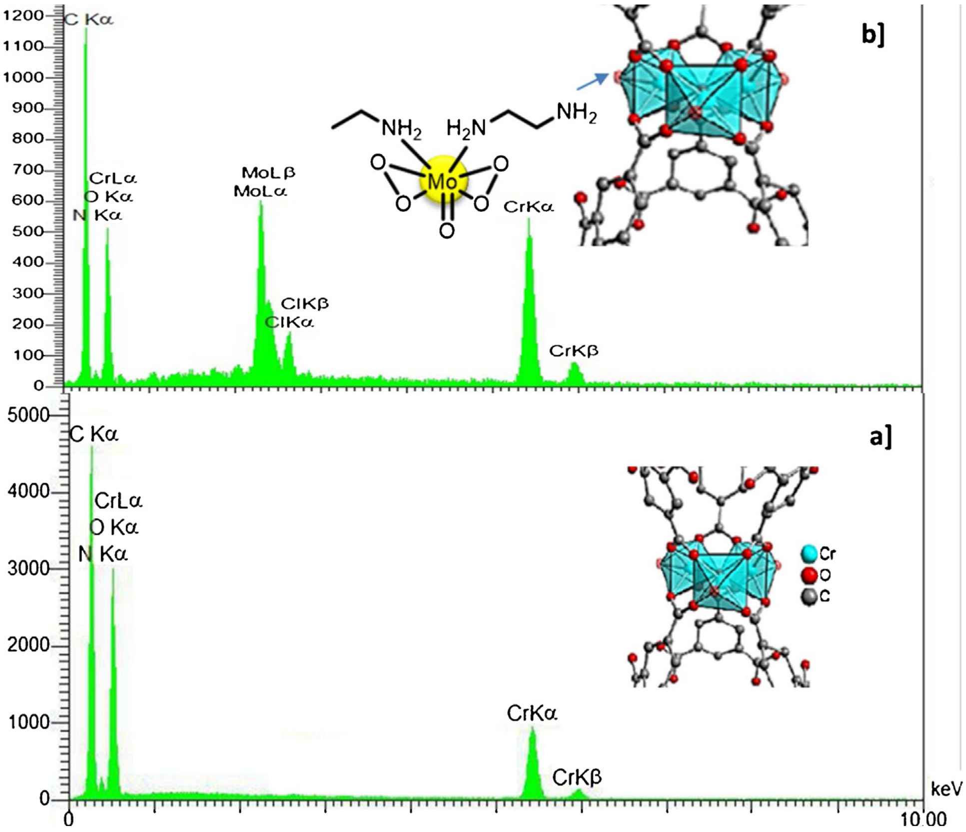


Fig. 5. a) SEM-EDX of a) MIL-100(Cr) and b) $MoO(O_2)_2$@En/MIL-100(Cr).

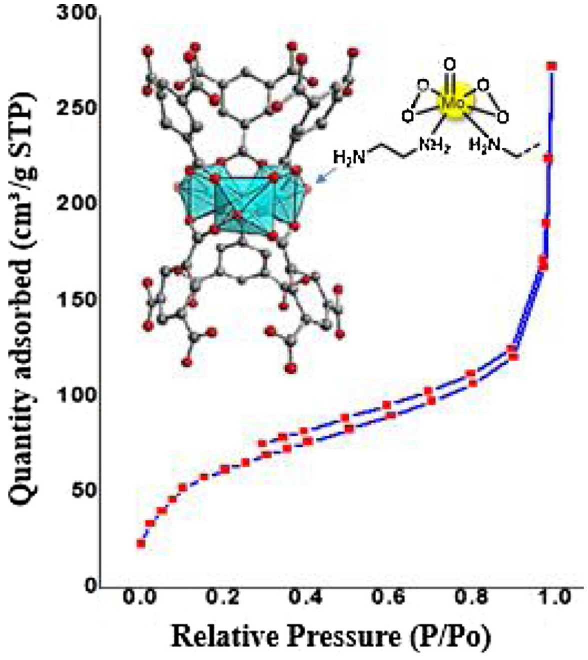


Fig. 6. Nitrogen sorption isotherms of $MoO(O_2)_2$@En/MIL-100(Cr).

and also a bit higher product yield, it was selected as an optimized solvent towards selective synthesis of sulfoxide (Fig. 8).

Table 1
Optimization conditions for the oxidation of model reaction.[a]

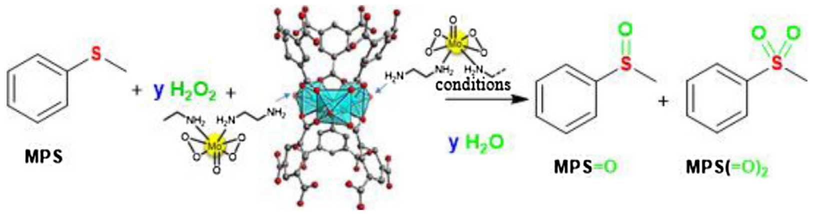
Entry	Temp. (°C)	H_2O_2 (eq.)	Yield (%)	
			Sulfoxide	Sulfone
1	25	4	75	25
2	40	4	50	50
3	70	4	40	60
4	100	4	30	70
5	25	2	93	7
6	25	6	45	55
7	25	8	31	69

[a] Reaction conditions: reaction conditions: 0.5 mmol of MPS, 0.04 g catalyst, H_2O (1 mL) during 30 min.

The temperature effect was also examined in the product yields. In this regard, temperatures including 25, 40, 70, 60, and 100 °C of model reaction were tested. One considerable point in this comparison was that the reaction at 25 °C with 4 eq. of H_2O_2 had lower reaction completion time for selective synthesis of sulfoxide with less than 25% of sulfone (Table 1). Amount of H_2O_2 oxidant was also optimized for the model oxidation reaction. Based on this study, the best amount of H_2O_2 for the selectivity of model reaction to generate sulfoxide was 2 mmol for each mmol of sulfide. Table 1, entry 1 and 5–7 represents the results for four different amount of H_2O_2 which was performed in the similar conditions.

In the next step, various aryl thioethers were incorporated to find out their reactivity and selectivity under the catalysis of $MoO(O_2)_2$@En/MIL-100(Cr). Certainly, aryl alkyl thioethers have a higher activity rather to their corresponding biaryl thioethers. This fact was also observed in this work. Accordingly, no significant difference were observed in the yields of various synthesized thioethers which were synthesized from an electron donor substitute (Table 2, entry 1–4). Upon optimization of reaction conditions, the scope of the reaction was subsequently extended to the utilization of heterocyclic thioethers (Table 2, entry 6 and 7).

Due to the fact that the nature of the bimetallic $MoO(O_2)_2$@En/MIL-100(Cr) as Mo/Cr-MOF may play an important role in the thioethers oxidation reaction, in comparison with same



Scheme 2. Benchmark model reaction over of $MoO(O_2)_2$@En/MIL-100(Cr).

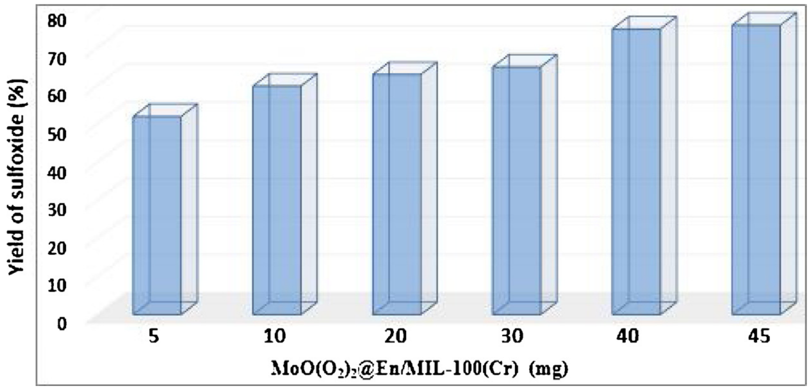


Fig. 7. Reaction conditions: reaction conditions: 0.5 mmol of MPS, 2 mmol of H_2O_2, in water (1 mL) at 25 °C during 30 min.

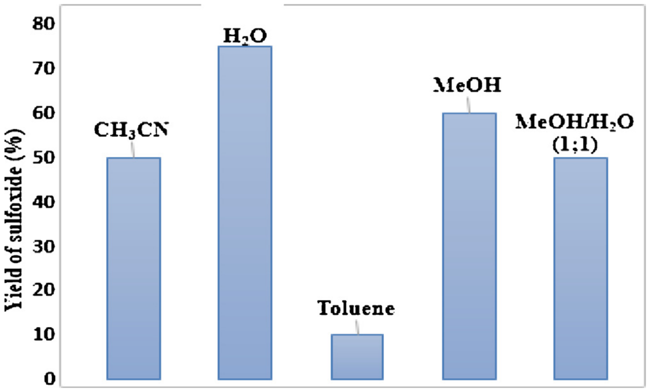


Fig. 8. Reaction conditions: reaction conditions: 0.5 mmol of MPS, 2 mmol of H_2O_2, 0.04 g catalyst, solvent (1 mL) at 25 °C during 30 min.

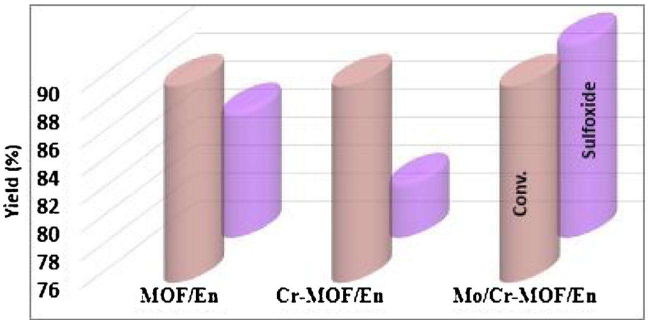
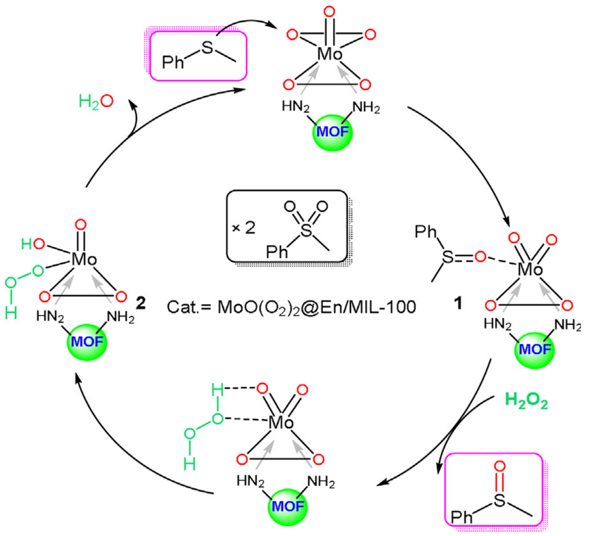


Fig. 9. Comparison reactivity of various MOFs.

structure, the initial reaction was carried out using MIL-100(Cr) and En/MIL-100(Cr) catalyst. The $MoO(O_2)_2$@En/MIL-100(Cr) as bimetallic Mo/Cr-MOF was assessed for its catalytic activity in the model reaction to produce of methyl phenyl sulfoxide as the principal product. When the model reaction was run using bimetallic Mo/Cr-MOF, the conversion product was 100% and sulfoxide obtained 90% yield during 30 min, instead for Cr-MOF/En and MOF/En the yield of sulfoxide was 85 and 80, respectively (Fig. 9).

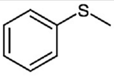
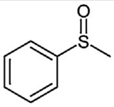
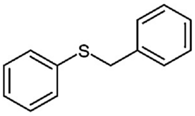
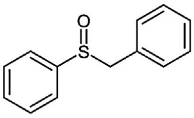
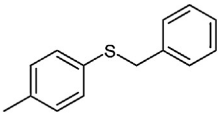
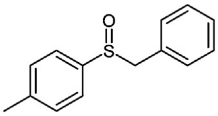
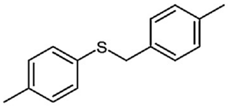
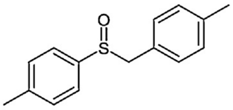
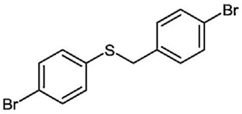
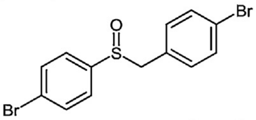
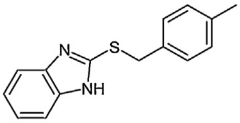
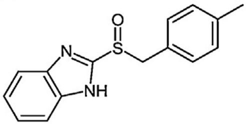
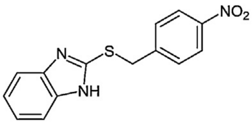
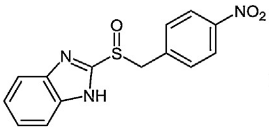


Scheme 3. Plausible mechanisms of oxodiperoxo Mo-mediated thioether oxidation.

A possible explanation mechanism for the thioether oxidation using H_2O_2 over the $MoO(O_2)_2$@En/MIL-100(Cr) catalyst was proposed in Scheme 3. Based on *literature* experimental and theoretical reports on oxidation process by oxodiperoxo mechanism [38,39], we propose that $MoO(O_2)_2$@En/MIL-100(Cr) easily reacts with thioether to form a dioxoperoxo Mo adduct **1**. Then, with H_2O_2 attach to **1**, the thioether oxide (sulfoxide) will remove the reaction cycle and a Mo-pendant OOH (Mo-OOH, **2**) adduct may undergo a cleavage of its O—OH bond to generate catalyst for next runs, in which MPS can be oxidized to the corresponding sulfoxide (or sulfone in repeat steps).

In this study, $MoO(O_2)_2$@En/MIL-100(Cr) could be recycled for 8 runs (Fig. 10). After completion of the reaction, the catalyst was

Table 2
Optimized reaction conditions for the oxidation of aromatic thioether.[a]

Entry	Substrate	Product	Time (min)	Conv. (%)	Yield sulfoxide (%)
1			30	100	93
2			35	100	92
3			30	100	94
4			60	100	93
5			130	90	83
6			120	92	81
7			30	86	56

[a] Reaction conditions: reaction scale (0.5 mmol).

recovered by centrifuge and washed with dichloromethane, dispersed and heated in 3 mL of fresh DMF at 100 °C for 2 h, activated under vacuum at 60 °C for 5 h, which was subsequently reused. No Mo was detected in reaction solution until 6th run (analyzing by atomic absorption spectroscopy), confirming the good stability of the systems under the investigated reaction conditions. However, after 6th runs, a significant drop in the yield can be observed. Fig. 10b shows SEM image of $MoO(O_2)_2$@En/MIL-100(Cr) in 8th run.

3. Experimental section

3.1. Material and apparatus

All reagents were purchased from Merck (Germany), Fluka (Switzerland) and Sigma-Aldrich and used without further purification. The crystalline phases of the nanoparticles were recognized by XRD measurements (Philips-PW1800 diffractometer). Homogeneous stirring was done by ultrasonic (Ultrasonic Homogenizer-model APU500 Advanced Equipment Engineering Company-Adeeco, Iran). Scanning electron microscopy (SEM) and SEM-EDS were recorded on VEGA3 TESCAN. Powder X-ray diffraction spectra was recorded on Philips PW1800.

3.2. Preparation of MIL-100(Cr)

MOF of MIL-100(Cr) and ethylene diamine grafted MIL-100(Cr) were synthesized according to Chang and Férey *et al.* [40] reported method. 1.2 g (12 mmol) of chromium trioxide, 2.52 g (11.99 mmol) of trimesic acid (H_3BTC), 12 mmol of hydrofluoric acid (HF, 40%) and 58 mL of deionized water were mixed in a Teflon-lined stainless steel autoclave and stirre at 298 K during 2 h and then kept at 493 K for 4 days. The resulting green solid was washed with water and dried at room temperature under air. The Cr- MOF was then characterized using a variety of different techniques.

3.3. Post-synthesis modification of MIL-100(Cr) with ethylene diamine (En)

The open metal site MOF of MIL-100(Cr) was activated in hot DMF (110 °C, 4 h) and then 16 h at room temperature at 393 K under vacuum for 12 h. The same activated method were done using ethanol and water in the solvent at 60 °C and 90 °C, respectively. Then, 0.1 g of MIL-100(Cr), activated at 473 K for 2 h, was suspended in 10 mL of anhydrous toluene and 1 mL of ethylene diamine was added to this suspension, and the mixture was stirred under Ar for

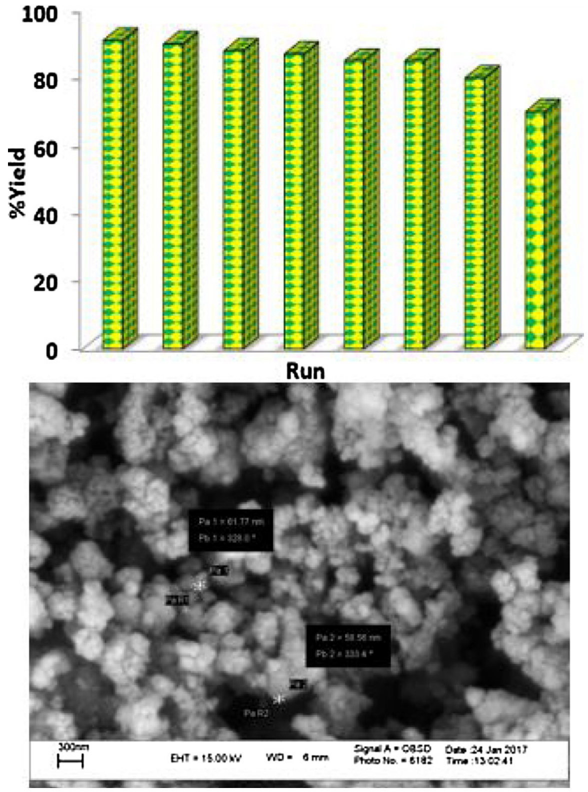


Fig. 10. a) Recyclability study of $MoO(O_2)_2$@En/MIL-100(Cr) (scale: 10 mmol) and b) its SEM image after 9th run.

16 h to facilitate amine grafting. The resulting En/MIL-100(Cr) solid was collected by filtration and repeatedly washed with acetone to remove the unreacted En, and then dried at 100 °C during 18 h.

3.4. En/MIL-100(Cr)-coordinately immobilized oxodiperoxo molybdenum complexes [$MoO(O_2)_2$@En/MIL-100(Cr)]

The obtained En/MIL-100(Cr) [40] was then incorporated with oxodiperoxo molybdenum complexes. 2 mmol of the oxodiperoxo molybdenum of $MoO(O_2)_2$·DMF was dissolved in 15 mL $CHCl_3$ followed by addition of 1 g of En/MIL-100(Cr) under vigorous stirring the suspension for 24 h. Finally, the solid was collected by filtering and Soxhlet with EtOH for 2 h and then after sonicate around 2 min in chloroform, it was dried at 60 °C at vacuum. According to atomic absorption analysis (AAS) of the composite, the Wt% of Mo in $MoO(O_2)_2$@En/MIL-100(Cr) was 20 per 100 mg of composite.

3.5. General procedure for the oxidation of thioethers

In a round-bottomed flask (25 mL) equipped with a magnetic stirrer, sulfide (0.5 mmol) was added to reaction flask in the presence of 1 mmol H_2O_2 (30% w/w) and $MoO(O_2)_2$@En/MIL-100(Cr) (0.04 g) in 1 mL water and stirred at 25 °C for an appropriate time (Table 2). After completion of the reaction, the product was extracted from reaction mixture with chloroform and then final product was obtained by evaporating chloroform from thioether oxide (sulfoxide).

4. Conclusion

In summary, oxodiperoxo complex of molybdenum coordinated ethylene diamine [$MoO(O_2)_2$/En] was successfully achieved on the cage of open metal site MOF of MIL-100(Cr). Under the optimized conditions, $MoO(O_2)_2$@En/MIL-100(Cr) as a new bifunctional Mo/Cr-MOF material was found to be an efficient nanoporous coordination polymer with hydrophobic nature which had high capacity for the catalysis of the green thioether oxidation reaction at room temperature in short reaction time. In this method, the reaction progress led to products, thioethers (sulfoxide), in high yields without side-products.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.11.003.

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