

<Supporting Information>

**Synthesis of highly stable Mo-Fe bimetallic metal-organic framework and its catalytic activity for
the selective oxidation of sulfides under mild conditions**

Xin Li^{a*}, Mohan Zu^a, Linzhuo Yan^a, Qiang Zhao^{a*}, Liu Liu^{b*}

^aCollege of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang, 473061, P. R. China.

^bNanyang Branch, Henan Provincial Tobacco Company, Nanyang, 473061, P. R. China.

*** Correspondence authors**

E-mail: lixin610207@126.com (X. Li)

E-mail: zhaoqiang0522@126.com (Q. Zhao)

E-mail: liuliu3281@126.com (L. Liu)

Table S1 Selected bond lengths (Å) and angles (°) for compound 1

| bond | distances (Å) | bond | distances (Å) |
|--------------|----------------------|--------------|----------------------|
| Mo(1)-O(6) | 1.699(5) | Fe(1)-O(1) | 2.134(5) |
| Mo(1)-O(7) | 1.760(5) | Fe(1)-O(7) | 2.150(5) |
| Mo(1)-O(8) | 1.802(5) | Fe(1)-N(1) | 2.165(6) |
| Mo(1)-O(5) | 1.814(5) | Fe(1)-O(5)#3 | 2.203(5) |
| Mo(2)-O(2)#1 | 1.735(5) | Fe(2)-O(4) | 2.059(5) |
| Mo(2)-O(3) | 1.757(5) | Fe(2)-O(5) | 2.094(5) |
| Mo(2)-O(4) | 1.772(5) | Fe(2)-O(8)#2 | 2.101(5) |
| Mo(2)-O(1)#2 | 1.818(5) | Fe(2)-N(2)#4 | 2.125(6) |
| Fe(1)-O(2) | 2.054(5) | Fe(2)-O(1)#3 | 2.136(5) |
| Fe(1)-O(3) | 2.077(5) | Fe(2)-O(8)#3 | 2.230(5) |

Symmetry code for 1: #1 $-1+x, -y-1, -z$; #2 $x+1, y, z$; #3 $1-x, -y, -z$; #4 $x+1, y+1, z+1$.

Table S2 The summarize of heterogeneous catalysis of Mo conationing species

| Entry | Catalysts | O | S | O:S | Sol. | T [°C] | t [min] | Conv ./% | Sel/ % | Ref. |
|-------|--|-------------------------------|-----|-----|--|-----------|------------|-------------|-----------|------|
| 1 | Mo ₈ O ₂₆ -calixarene | H ₂ O ₂ | 0.2 | 1 | CH ₃ CN | 50 | 40 | 81 | 91 | 1 |
| 2 | Cs ₄ [M(H ₂ O) ₄][PMo ₆ O ₂₁ (PABA) ₃] ₂ ·nH ₂ O (M = Co, Mn, Ni, Zn; PABA = p-aminobenzoic acid) | H ₂ O ₂ | 0.2 | 1.2 | CH ₃ OH | 25 | 20 | 99 | 98 | 2 |
| 3 | [Co(BBPTZ) ₃][HPMo ₁₂ O ₄₀]·24H ₂ O BBPTZ=4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl] | TBHP | 0.4 | 3 | CH ₂ Cl ₂ | 50 | 15 | 100 | | 3 |
| 4 | [Mn(TMR4A)(H ₂ O) ₄] [Mo ₆ O ₁₉]·0.5CH ₃ CH ₂ OH·H ₂ O (1), [Ni(TMR4A)(H ₂ O) ₄][Mo ₆ O ₁₉]·0.5CH ₃ CH ₂ OH·H ₂ O (2), [Zn(TMR4A)(H ₂ O) ₄][Mo ₆ O ₁₉]·0.5CH ₃ CH ₂ OH·H ₂ O (3), [Co ₂ (TMR4A) ₂ (H ₂ O) ₄ (β-Mo ₈ O ₂₆)]·CH ₃ CN·12H ₂ O (4) | TBHP | 0.4 | 1 | CH ₂ Cl ₂ | 40 | 60 | 99 | | 4 |
| 5 | [Co ₂ Mo ₁₀ H ₄ O ₃₈] ₆ (en)[Cu ₃ (ptz) ₄ (H ₂ O) ₄][Co ₂ Mo ₁₀ H ₄ O ₃₈]·24H ₂ O (1), (Hbim) ₂ {[Cu(bim) ₂ (H ₂ O) ₂] ₂ {Co ₂ Mo ₁₀ H ₄ O ₃₈ }}·5H ₂ O (2), H ₂ [Cu(dpdo) ₃ (H ₂ O) ₄][{Cu ₂ (dpdo) ₃ (H ₂ O) ₄ (CH ₃ CN)} ₂ {Co ₂ Mo ₁₀ H ₄ O ₃₈ }] ₂ ·9H ₂ O (3), (H ₂ bpp) ₄ {[Cu(H ₂ O) ₂]{NaCo ₂ Mo ₁₀ H ₄ O ₃₈ }] ₂ ·10H ₂ O (4) | TBHP | 0.2 | 2 | CH ₃ CN | 40 | 240 | 95 | 95 | 5 |
| 6 | [MoO ₃ (2,2'-bipy)] _n | TBHP | 1 | 3 | CH ₂ Cl ₂ | 20 | 120 | 97 | 99 | 6 |
| 7 | M-Anderson-COF (MMo ₆ , M = Mn ³⁺ , Co ³⁺ , Fe ³⁺) | H ₂ O ₂ | 1 | 5 | CH ₃ CN | 50 | 60 | 100 | 100 | 7 |
| 8 | K ₄ H ₅ [Ln ₃ (H ₂ O) ₁₄ {(Mo ₈ O ₂₄)(O ₃ PCH ₂ COO) ₃ }] ₂ ·23H ₂ O (Ln = Gd (1Gd), Tb (2Tb), Dy (3Dy)) | H ₂ O ₂ | 1 | 2 | CH ₃ CN | 50 | 60 | 100 | 100 | 8 |
| 9 | Na ₂ H ₂ [Mo ₄ O ₁₂ (C ₈ H ₁₇ O ₅ N) ₂] ₂ ·10H ₂ O (1), Na ₂ [M(Bis-tris)(H ₂ O)] ₂ [Mo ₇ O ₂₄]·10H ₂ O [M = Cu, Ni, Co, Zn, Bis-tris =2,2-Bis(hydroxymethyl)-2,2',2''-nitrilotriethanol], | H ₂ O ₂ | 0.7 | 1.5 | C ₂ H ₅ OH | 50 | 15 | 99 | 95 | 9 |
| 10 | [Mo(O)(O ₂) ₂ (Mepz) ₂] | H ₂ O ₂ | 1 | 1 | [C ₄ mim][PF ₆] | 20 | 60 | 80 | 96 | 10 |

| | | | | | | | | | | |
|----|---|----------|-----|------|------------|----|-----|-----|-----|-----------|
| 11 | $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$ | H_2O_2 | 1 | 1 | H_2O | 25 | 30 | 95 | | 11 |
| 12 | $Fe_3O_4@Si-APFSB-MoO_2$ | H_2O_2 | 10 | 1.5 | H_2O | 55 | 5 | 99 | 95 | 12 |
| 13 | PMoCh | H_2O_2 | 5 | 4 | H_2O | 25 | 65 | 97 | 100 | 13 |
| 14 | ECS- $MoO_2(acac)_2$ | TBHP | 1 | 1.5 | C_2H_5OH | 25 | 360 | 91 | 97 | 14 |
| 15 | [CMK-3/Im/ MoO_4^{2-}] | H_2O_2 | 1 | 2 | CH_3CN | 25 | 7 | 96 | | 15 |
| 16 | MFO@NS- $MoOO_2$ | H_2O_2 | 1 | 1.5 | H_2O | 55 | 5 | 98 | 95 | 16 |
| 17 | GO/[Fe_3O_4]/ $Co_3O_4-MoO_3$ | H_2O_2 | 2 | 2.5 | CH_3CN | 40 | 10 | 100 | 57 | 17 |
| 18 | $Fe_3O_4@SiO_2-APTES$ | H_2O_2 | 1 | 5 | CH_3CN | 40 | 50 | 100 | 78 | 18 |
| 19 | SBA-15@AP-LAEB- $Mo(VI)O_2$ | H_2O_2 | 1 | 3 | C_2H_5OH | 25 | 120 | 100 | 99 | 19 |
| 20 | (L) $Mo(VI)O_2@SBA-15$ | H_2O_2 | 1 | 1 | CH_3CN | 26 | 180 | 100 | 85 | 20 |
| 21 | $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$ | H_2O_2 | 1 | 1 | H_2O | 25 | 30 | 95 | 100 | 21 |
| 22 | [$MoO_2(O_2)(L)_2$] ₂ --MR [L = valine (MRVMo), alanine (MRAMo)] | H_2O_2 | 5 | 2 | CH_3OH | 25 | 40 | 98 | 100 | 22 |
| 23 | $TiO_2/AA/MoO_2$ | H_2O_2 | 1 | 2 | CH_3OH | 70 | 30 | 100 | 100 | 23 |
| 24 | $Fe_3O_4@SiO_2-NH_2-Mo$ | UHP | 0.4 | 0.45 | CH_3OH | 25 | 30 | 86 | 92 | 24 |
| 25 | [$Fe_2(4,4'-bpy)Mo_2O_8$] $\cdot 3H_2O$ | H_2O_2 | 1 | 1 | CH_3OH | 25 | 60 | 96 | 98 | This work |

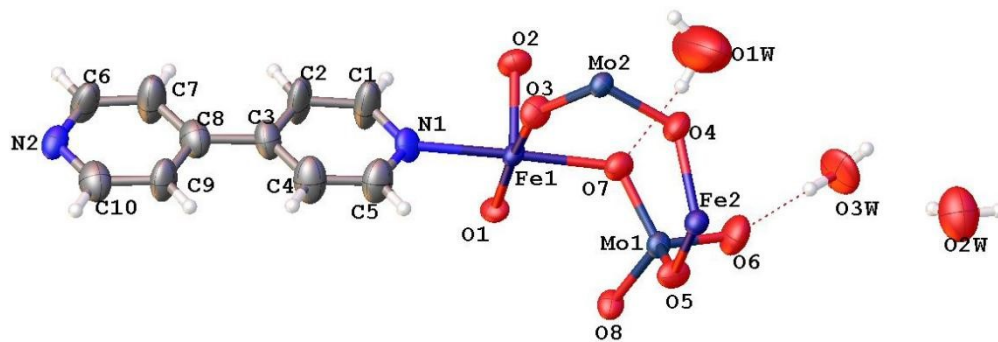


Fig. S1. Asymmetry unit structure of **1** with thermal ellipsoids set at 80% probability level.

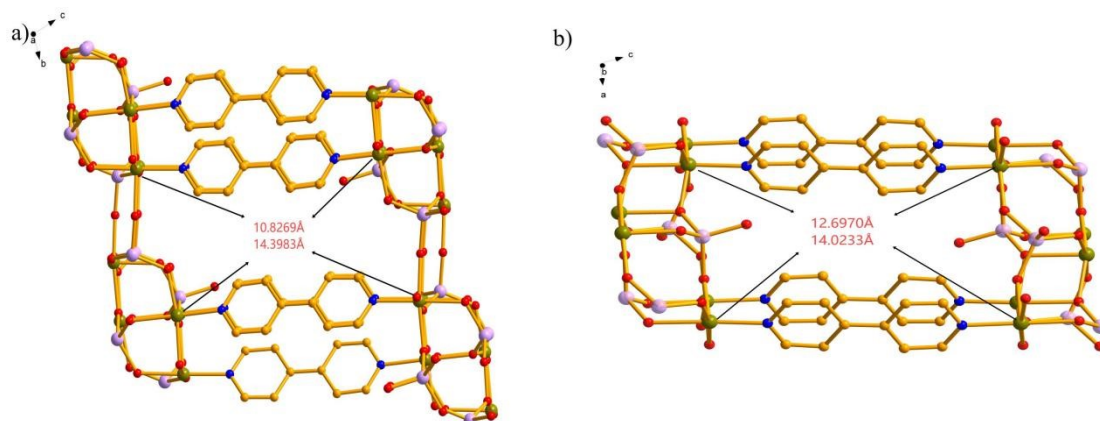


Fig. S2. a) The dimensions of the channel and pore size of compound 1 along axis a. b) The dimensions of the channel and pore size of compound 1 along axis b.

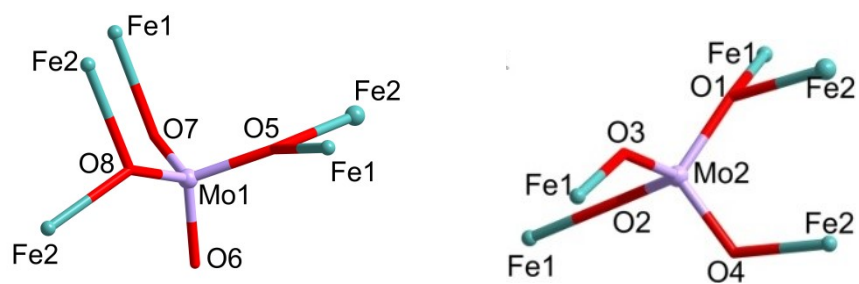


Fig. S3. Crystallographically fashions of the [MoO₄]²⁻ linker with iron atom in 1.

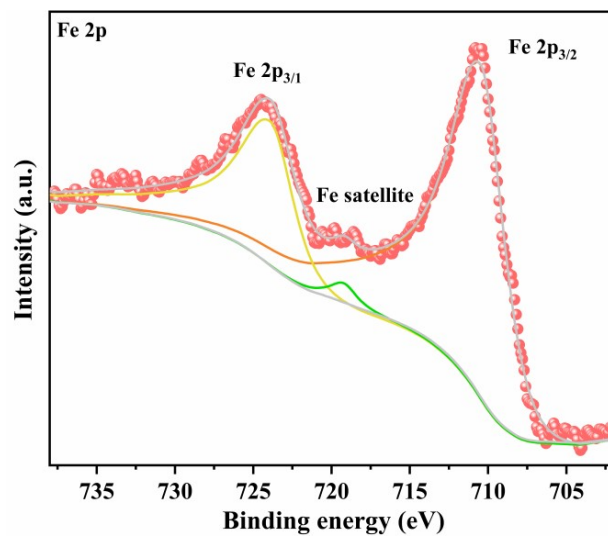


Fig. S4. The Fe 2p XPS spectra of compound 1.

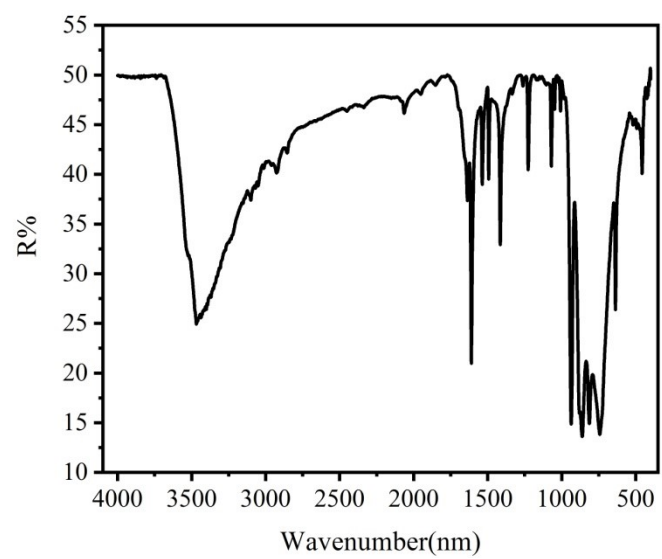


Fig. S5. IR spectra of compound 1

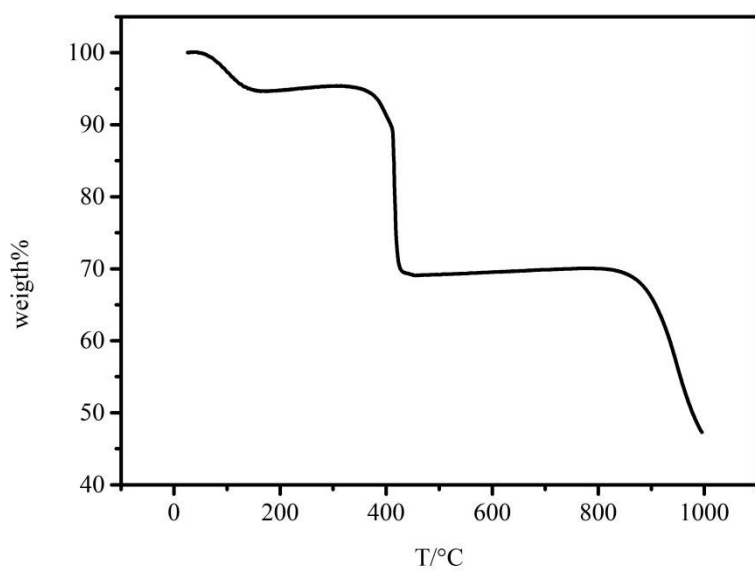


Fig. S6. The TGA of the 1.

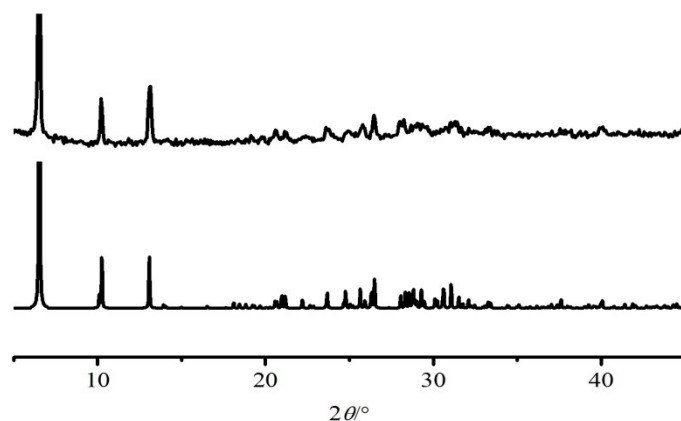


Fig. S7. The experimental (top) and simulated (bottom) X-ray powder diffraction (XRPD) patterns of 1, showing that of the bulk product is in good agreement with the calculated one based on the single-crystal X-ray diffraction.

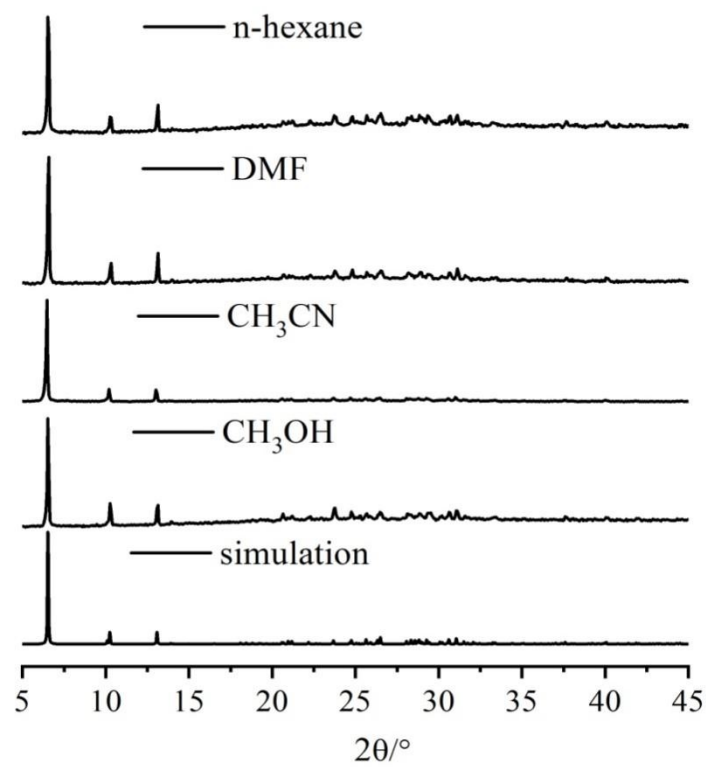


Fig. S8. The XRD of the sample immersed in varies solution for 2 days.

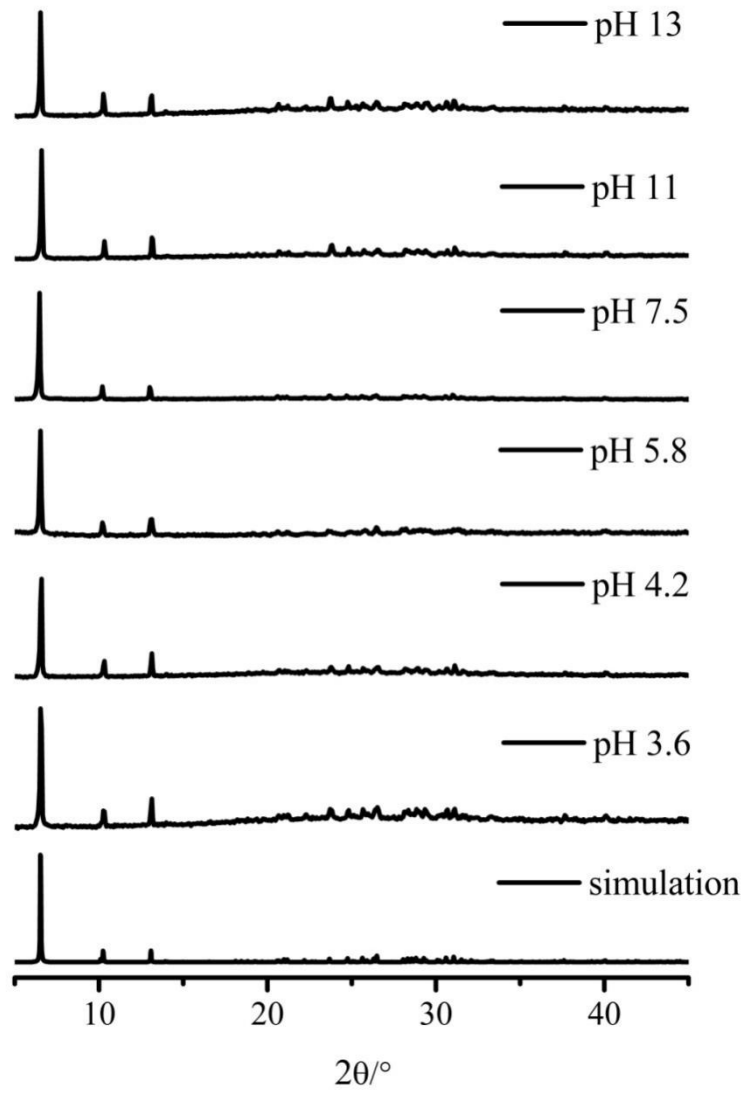


Fig. S9. The XRD of the sample immersed in varies pH solution for 2 days.

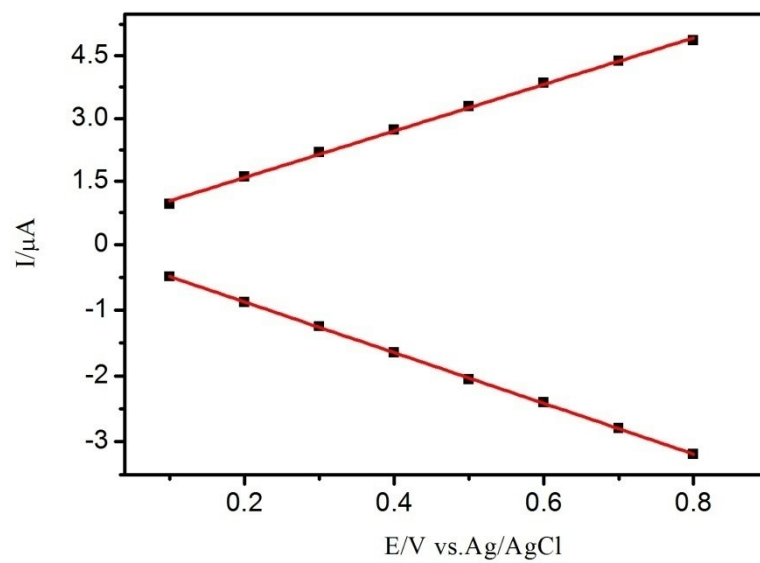


Fig. S10. The Diagram shows plots of the anodic (up) and the cathodic (down) peak currents for I-I' against.

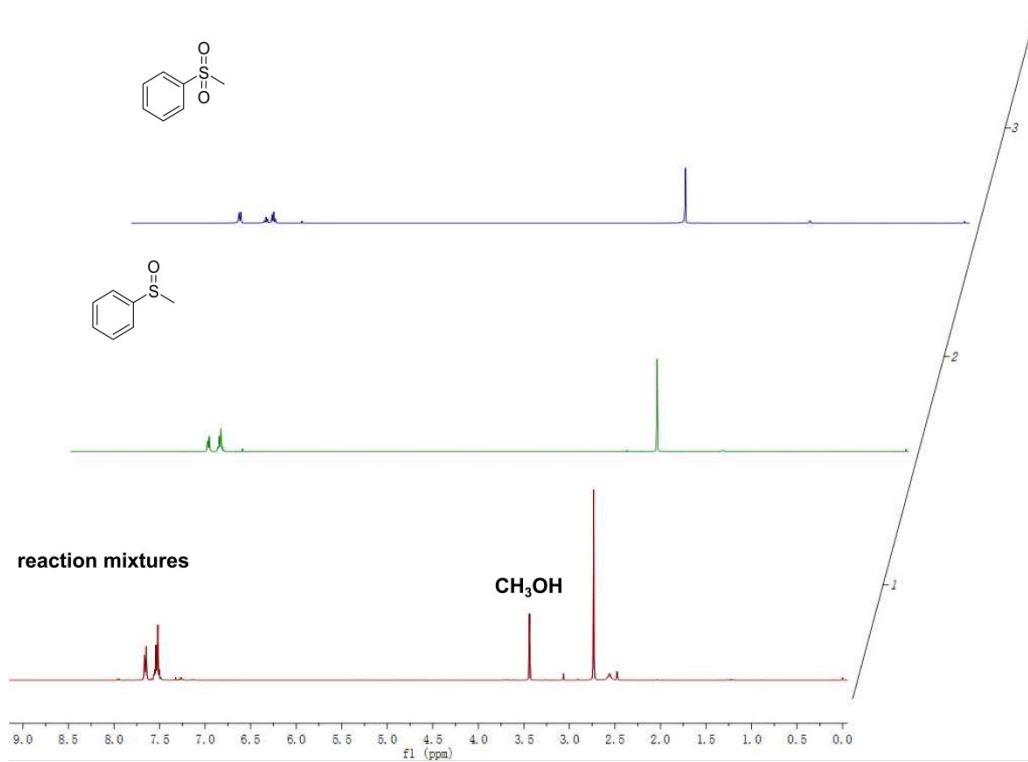


Fig. S11. The $^1\text{H-NMR}$ of the reaction mixtures after reaction.

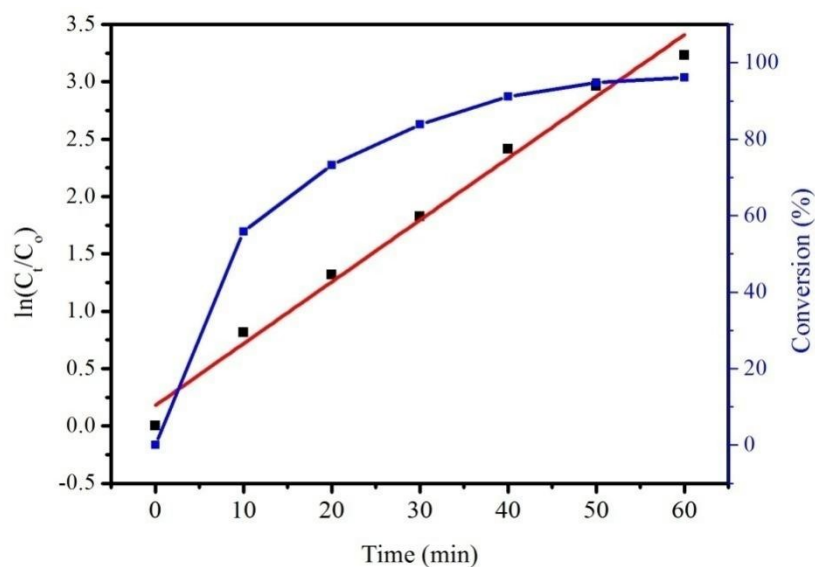


Fig. S12. Kinetics for oxidation of methyl phenyl sulfide using catalyst 1 at room temperature. C_0 and C_t represent the concentrations of reactant initially and at time t , respectively. Equation: $\ln(C_t/C_0) = -kt$. Kinetic studies stated that the catalytic reaction follow first-order dependences [25].

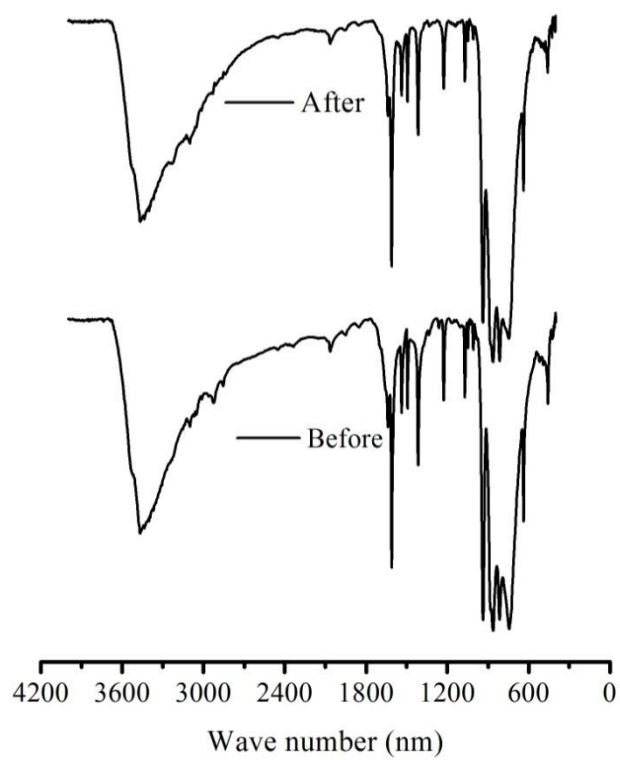


Fig. S13. IR spectra of the catalyst 1 before and after reaction

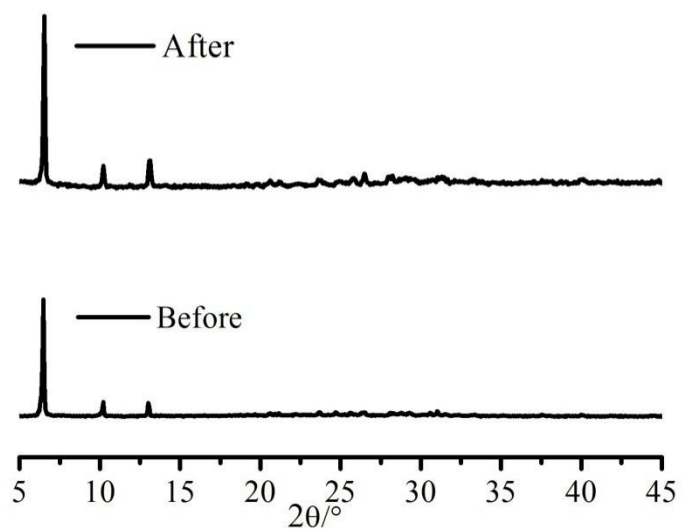


Fig. S14. XRD for the catalyst 1 before and after reaction.

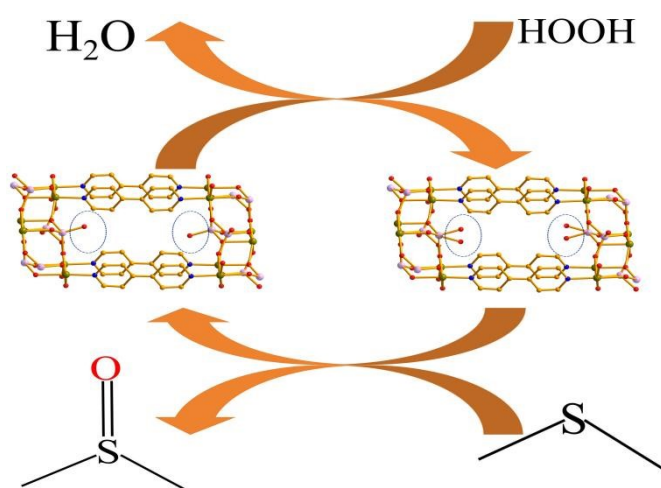


Fig. S15. Proposed catalytic mechanism for the sulfoxidation reaction using compound **1** and H_2O_2 as an oxidant.

References

- [1] S. Meninno, A. Parrella, G. Brancatelli, S. Geremia, C. Gaeta, C. Talotta, P. Neri, A. Lattanzi, Polyoxomolybdate-calix[4]arene hybrid: a catalyst for sulfoxidation reactions with hydrogen peroxide, *Org. Lett.* **17** (2015) 5100–5103.
- [2] H.Y. An, Y.J. Hou, S.Z. Chang, J. Zhang, Q.S. Zhu, Highly efficient oxidation of various thioethers catalyzed by organic ligand-modified polyoxomolybdates, *Inorg. Chem. Front.* **7** (2020) 169–176.
- [3] X.L. Hao, Y.Y. Ma, H.Y. Zang, Y.H. Wang, Y.G. Li, E.B. Wang, A polyoxometalate-encapsulating cationic metal–organic framework as a heterogeneous catalyst for desulfurization, *Chem. Eur. J.* **21** (2015) 3778 – 3784.
- [4] M.Y. Yu, J. Yang, T.T. Guo, J.F. Ma, Efficient catalytic oxidative desulfurization toward thioether and sulfur mustard stimulant by polyoxomolybdate–resorcin[4]arene based metal–organic materials, *Inorg. Chem.* **59** (2020) 4985–4994.
- [5] H.Y. An, Y.J. Hou, L. Wang, Y.M. Zhang, W. Yang, S.Z. Chang, Evans–showell-type polyoxometalates constructing high dimensional inorganic–organic hybrid compounds with copper–organic coordination complexes: synthesis and oxidation catalysis, *Inorg. Chem.* **56** (2017) 11619–11632.
- [6] I. Tosia, C. Vurchio, M. Abrantes, I.S. Gonçalves, M. Pillinger, F. Cavani, F.M. Cordero, A. Brandi, $[\text{MoO}_3(2,2'\text{-bipy})]_n$ catalyzed oxidation of amines and sulfides, *Catal. Commun.* **103** (2018) 60–64.
- [7] R. Ma, N.F. Liu, T.T. Lin, T.B. Zhao, S.L. Huang, G.Y. Yang, Anderson polyoxometalate built-in covalent organic frameworks for enhancing catalytic performances, *J. Mater. Chem. A* **8** (2020) 8548–8553.
- [8] J.W. Wang, Y.J. Niu, M. Zhang, P.T. Ma, C. Zhang, J.Y. Niu, J.P. Wang, Organophosphonate-functionalized lanthanopolyoxomolybdate: synthesis, characterization, magnetism, luminescence, and catalysis of H_2O_2 -based thioether oxidation, *Inorg. Chem.* **57** (2018) 1796–1805.
- [9] Y. Zhang, W.D. Yu, B. Li, Z.F. Chen, J. Yan, Discovery of a new family of polyoxometalate-based hybrids with improved catalytic performances for selective sulfoxidation: the synergy between classic heptamolybdate anions and complex cations, *Inorg. Chem.* **58** (2019)

14876–14884.

[10] C.J. Carrasco, F. Montilla, E. Álvarez, C. Mealli, G. Mancac, A. Galindo, Experimental and theoretical insights into the oxodiperoxomolybdenum-catalysed sulphide oxidation using hydrogen peroxide in ionic liquids, *Dalton Trans.* 43 (2014) 13711–13730

[11] R.D. Chakravarthy, V. Ramkumar, D.K. Chand, A molybdenum based metallomicellar catalyst for controlled and selective sulfoxidation reactions in aqueous medium, *Green Chem.* 16 (2014) 2190–2196.

[12] A. Bezaatpour, E. Askarizadeh, S. Akbarpour, M. Amiria, B. Babaei, Green oxidation of sulfides in solvent-free condition by reusable novel Mo(VI) complex anchored on magnetite as a high-efficiency nanocatalyst with eco-friendly aqueous H₂O₂, *Mol. Catal.* 436 (2017) 199–209.

[13] K. Ahmed, Ga. Saikia, P. Begum, S.R. Gogoi, M. Sharma, H. Talukdar, N.S. Islam, Selective and green sulfoxidation in water using a new chitosan supported Mo(VI) complex as heterogeneous catalyst, *ChemistrySelect* 3 (2018) 12563–12575.

[14] M. Hong, J.M. Yan, Immobilized molybdenum acetylacetonate complex on expanded starch for chemoselective oxidation of sulfides to sulfoxides with t-BuOOH at room temperature, *Phosphorus. Sulfur. Silicon.* 192 (2017) 985–988.

[15] F.H. Eshbala, A. Sedrpoushan, B. Breita, F. Mohanazadeh, H. Veisi, Ionic-liquid-modified CMK-3 as a support for the immobilization of molybdate ions (MoO₄²⁻): Heterogeneous nanocatalyst for selective oxidation of sulfides and benzylic alcohols. *Mater. Sci. Eng. C.* 110 (2020) 110577.

[16] B. Babaei, A. Bezaatpour, H. Basharnavaz, Robust and fast oxidation of sulfides by immobilized Mo(VI) complex on magnetic nanoparticles in solvent-free condition, *Polyhedron* 179 (2020) 114382.

[17] M. Khoshroo1, H.H. Monfared, Oxidation of sulfides with H₂O₂ catalyzed by impregnated graphene oxide with Co–Cu–Zn doped Fe₃O₄/Co₃O₄–MoO₃ nanocomposite in acetonitrile, *J Inorg Organomet Polym.* 27 (2017) 165–175.

[18] A. Bayat, M.S. Fard, M.M. Hashemi, Selective oxidation of sulfides to sulfoxides by a molybdate-based catalyst using 30% hydrogen peroxide, *Catalysis Communications* 52 (2014) 16–21.

- [19] I. Saberikia, E. Safaei, B. Karimi, Y. Lee, Oxygenation of sulfides catalysed by SBA-15-immobilized molybdenum(VI) complex of a bis(phenol) diamine ligand using aqueous hydrogen peroxide as a green oxidant, *Appl. Organometal. Chem.* (2019) pp e4304.
- [20] A. Lazar, W.R. Thielb, A.P. Singh, Synthesis and characterization of 3-[N,N'-bis-3-(salicylidenamino)ethyltriamine] Mo(VI)O₂@SBA-15: a highly stable and reusable catalyst for epoxidation and sulfoxidation reactions, *RSC Adv.* 4 (2014) 14063–14073.
- [21] R.D. Chakravarthy, V. Ramkumar, D.K. Chand, A molybdenum based metallomicellar catalyst for controlled and selective sulfoxidation reactions in aqueous medium, *Green Chem.*, 16 (2014) 2190–2196.
- [22] J.J. Boruah, S.P. Das, S.R. Ankireddy, S.R. Gogoi, N.S. Islam, Merrifield resin supported peroxomolybdenum(VI) compounds: recoverable heterogeneous catalysts for the efficient, selective and mild oxidation of organic sulfides with H₂O₂, *Green Chem.* 15 (2013) 2944–2959.
- [23] M. Jafarpour, A. Rezaeifard, M. Ghahramaninezhad, F. Feizpour, Dioxomolybdenum(VI) complex immobilized on ascorbic acid coated TiO₂ nanoparticles catalyzed heterogeneous oxidation of olefins and sulfides, *Green Chem.* 17 (2015) 442–452.
- [24] H. Keypour, M. Balali, M.M. Haghdoost, M. Bagherzadeh, Mo(VI) complex supported on Fe₃O₄ nanoparticles: magnetically separable nanocatalysts for selective oxidation of sulfides to sulfoxides, *RSC Adv.* 5 (2015) 53349–53356.
- [25] R. Wan, P.P. He, Z. Liu, X.Y. Ma, P.T. Ma, V. Singh, C. Zhang, J.Y. Niu, J.P. Wang, A lacunary polyoxovanadate precursor and transition-metal sandwiched derivatives for catalytic oxidation of sulfides, *Chem. Eur. J.* 26 (2020) 1–8.