

Supporting Information

A novel polyoxovanadate-based Co–MOF: highly efficient and selective oxidation of mustard gas simulant by two-site synergetic catalysis

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Table of Contents

1. Crystallographic Data and Structure Refinements.....	S3
2. BVS Results.....	S4
3. XPS Spectra of V-Co-MOF and V-Ni-MOF.....	S4
4. PXRD Patterns of V-Co-MOF and V-Ni-MOF.....	S5
5. FTIR Spectra of V-Co-MOF and V-Ni-MOF.....	S5
6. TGA Curves of V-Co-MOF and V-Ni-MOF.....	S6
7. BET Analysis of V-Co-MOF and V-Ni-MOF.....	S6
8. Mass Spectrum of CEESO.....	S7
9. ¹ H-NMR Spectra of CEES Oxidation Process with V-Co-MOF as Catalyst.....	S7
10. The influence of the Quantity of Catalyst and Oxidant for CEES Oxidation.....	S8
11. Kinetic Analysis of CEES Oxidation for V-Co-MOF and V-Ni-MOF.....	S8
12. PXRD Patterns of NaK{V ₂ O ₆ }.....	S9
13. FTIR Spectra of CEES Molecules Absorbed on V-Co-MOF and V-Ni-MOF.....	S9
14. XPS Spectra of Co ²⁺ in V-Co-MOF-A and Ni ²⁺ in V-Ni-MOF-A.....	S10
15. FTIR Spectra and Raman Spectra of V-Co-MOF-treating with 30% H ₂ O ₂	S10
16. Comparison of CEES Catalytic Oxidation by Different Catalysts.....	S11
17. References.....	S12

1. Crystallographic Data and Structure Refinements

Table S1. Crystallographic data and structure refinements of V-Co-MOF and V-Ni-

MOF

Name	V-Co-MOF	V-Ni-MOF
Empirical formula	C ₁₂ H ₁₀ CoN ₄ O ₆ V ₂	C ₁₄ H ₂₂ N ₆ O ₈ V ₂ Ni
Formula weight	467.05	562.96
Temperature (K)	298	298
Wave length (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
a (Å)	15.592(5)	9.3037(4)
b (Å)	5.5370(17)	24.5253(9)
c (Å)	19.668(6)	9.8451(3)
α (deg)	90	90
β (deg)	111.991(6)	112.9020(10)
γ (deg)	90	90
Volume (Å ³)	1574.4(8)	2069.33(13)
Z, D _{calc} (Mg/m ³)	4, 1.970	4, 1.807
Absorption coefficient (mm ⁻¹)	2.243	1.841
F (000)	924.0	1144.0
Crystal size (mm ³)	0.25 × 0.23 × 0.22	0.21 × 0.2 × 0.19
θ range (deg)	4.466 to 50.178	4.788 to 50.122
index range (deg)	-18 ≤ h ≤ 11, -6 ≤ k ≤ 6, -23 ≤ l ≤ 23	-11 ≤ h ≤ 11, -29 ≤ k ≤ 29, -11 ≤ l ≤ 11
Reflections collected / unique	4372 / 1401 [Rint = 0.0289]	19036 / 3660 [Rint = 0.0306]
Data / restraints / parameters	1401 / 0 / 114	3660 / 0 / 286
Goodness-of-fit on F ²	1.044	1.105
R ₁ , wR ₂ (I > 2σ(I))	0.0383, 0.0824	0.0335, 0.0863
R ₁ , wR ₂ (all data)	0.0497, 0.0876	0.0372, = 0.0884
Largest diff. peak and hole (e Å ⁻³)	0.35, -0.43	0.41, -0.68

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \left[\frac{\sum [w (F_o^2 - F_c^2)^2]}{\sum [w (F_o^2)^2]} \right]^{1/2}$$

2. BVS Results

Table S2. BVS results for the vanadium ions, cobalt ion and nickel ions in V-Co-MOF and V-Ni-MOF.

Metal site	BVS cacl.	Assigned O.S.
V-Co-MOF		
V1	5.363	5
Co1	2.234	2
V-Ni-MOF		
V1	5.218	5
V2	5.234	5
Ni1	2.109	2

3. XPS Spectra of V-Co-MOF and V-Ni-MOF

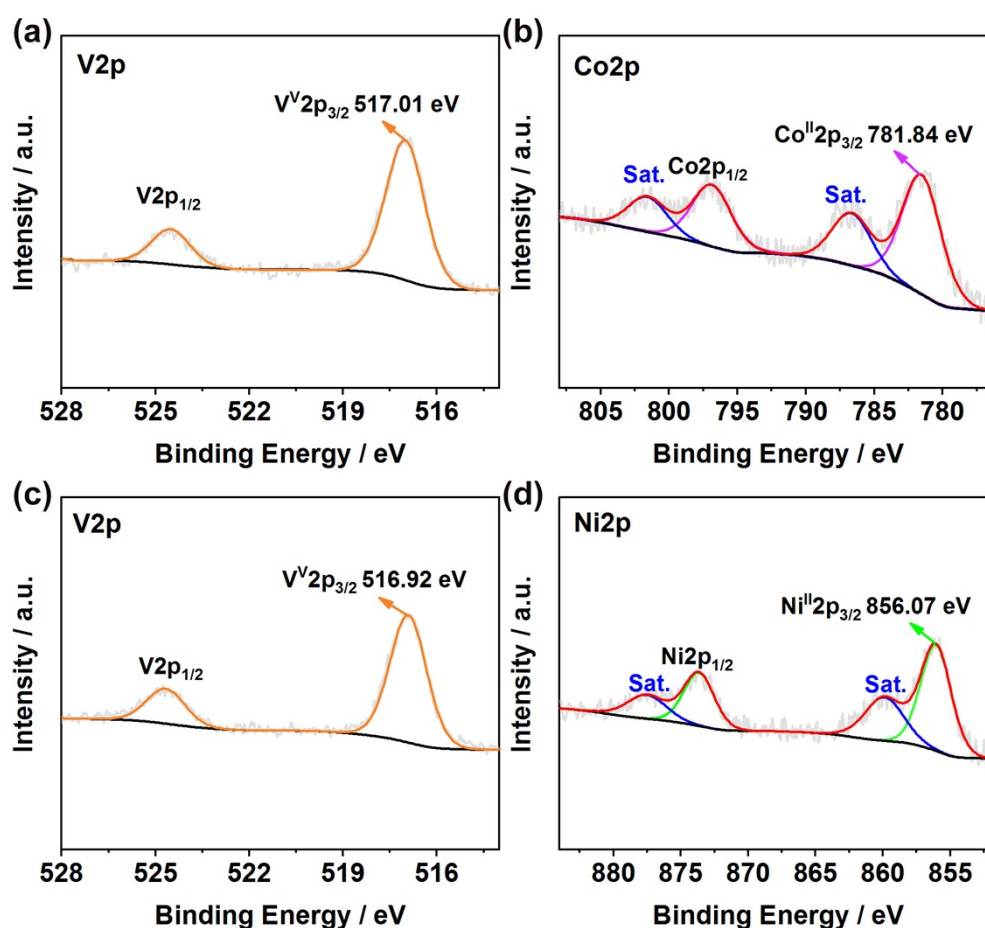


Figure S1. (a, b) XPS spectra of V ions and Co ions in V-Co-MOF. (c, d) XPS spectra of V ions and Ni ions in V-Ni-MOF.

4. PXRD Patterns of V-Co-MOF and V-Ni-MOF

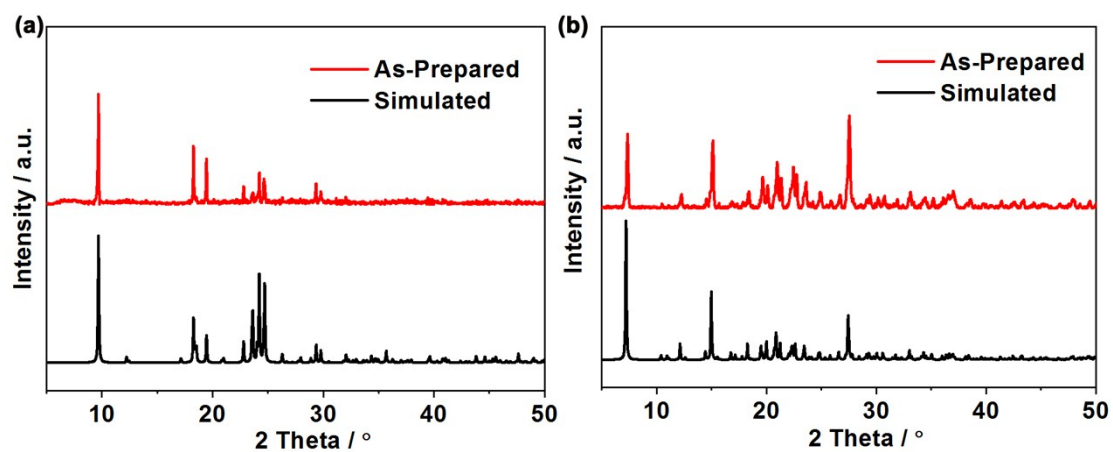


Figure S2. PXRD patterns of V-Co-MOF and V-Ni-MOF.

5. FTIR Spectra of V-Co-MOF and V-Ni-MOF

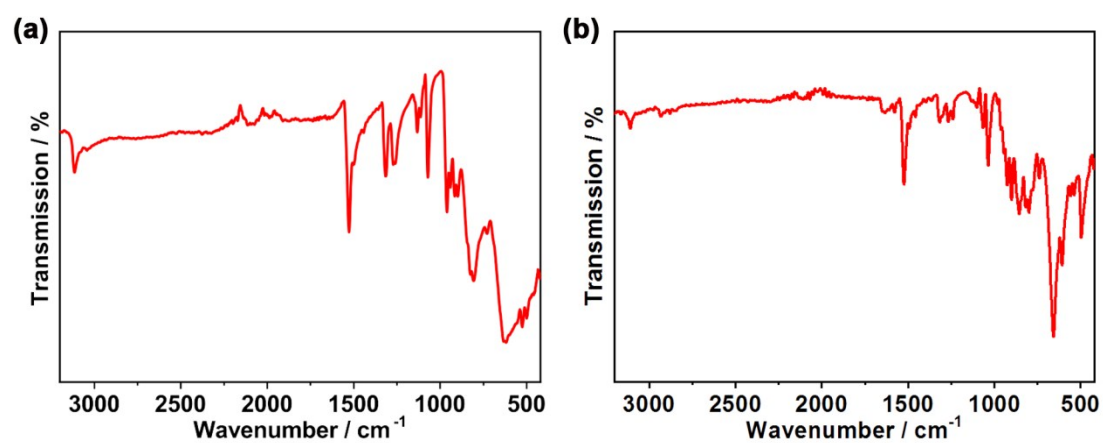


Figure S3. (a) The FTIR spectrum of V-Co-MOF. (b) The FTIR spectrum of V-Ni-MOF.

6. TGA Curves of V-Co-MOF and V-Ni-MOF

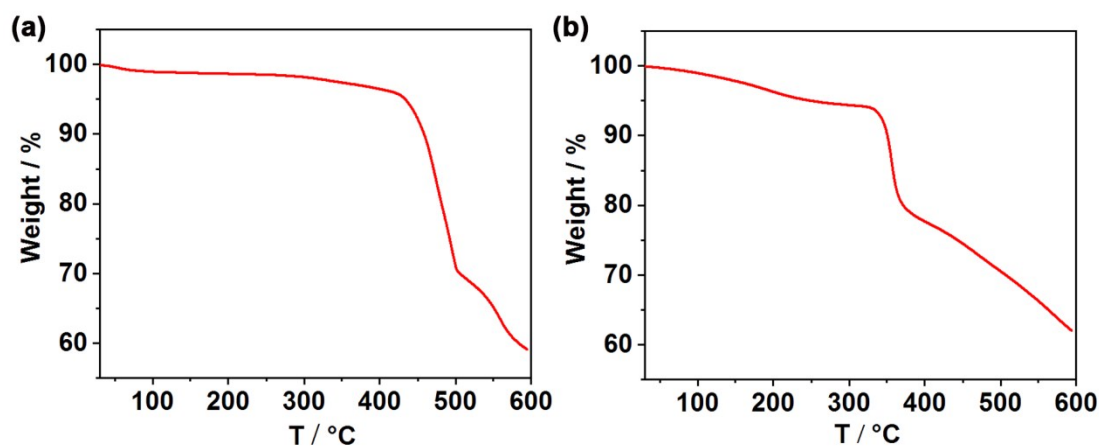


Figure S4. (a) The TGA curve of V-Co-MOF. (b) The TGA curve of V-Ni-MOF.

7. BET Analysis of V-Co-MOF and V-Ni-MOF

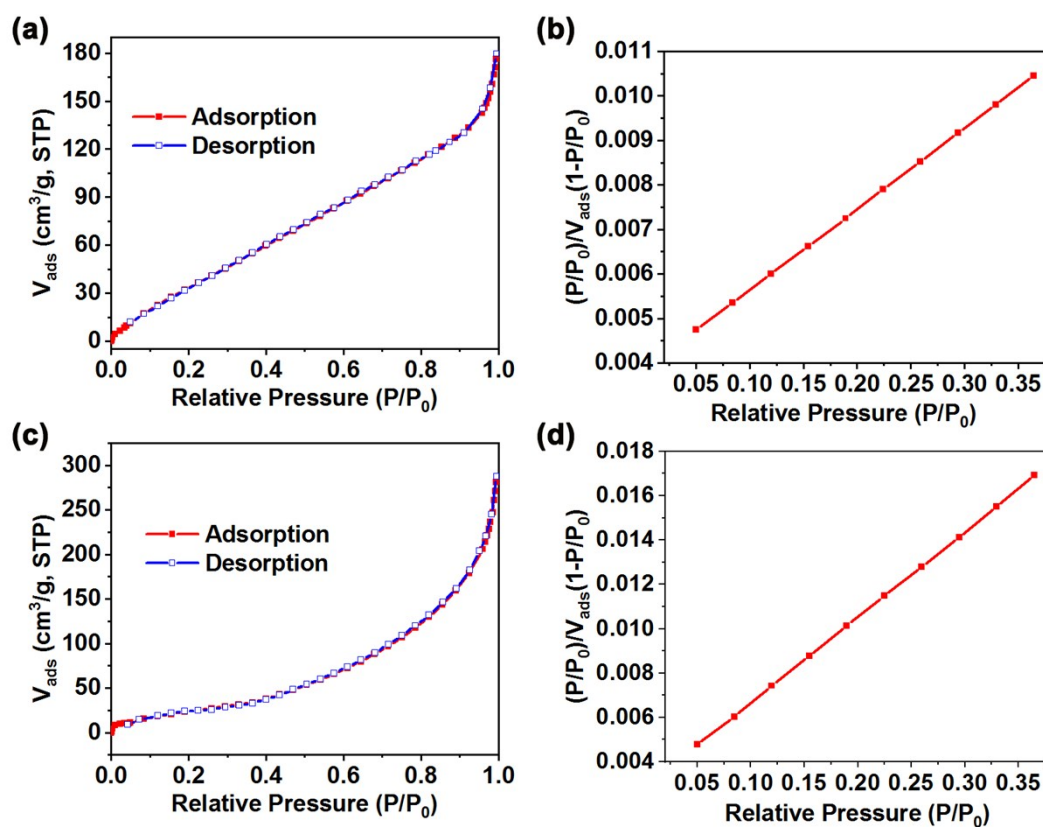


Figure S5. BET analysis of V-Co-MOF (a, b) and V-Ni-MOF (c, d). The N₂ adsorption / desorption isotherms were measured at 77K ($P_0 = 101$ kPa).

8. Mass Spectrum of CEESO

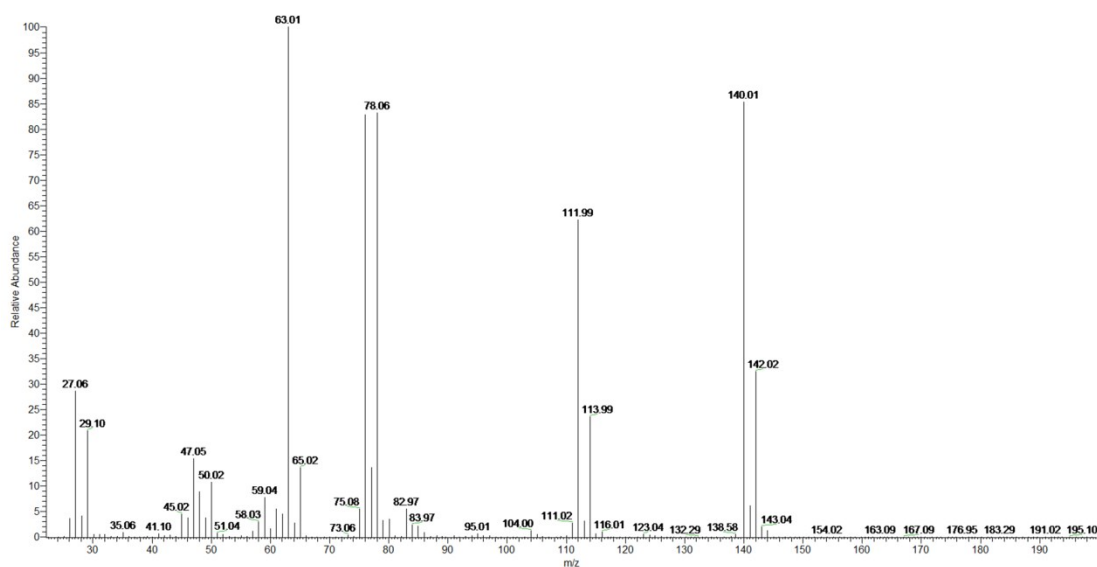


Figure S6. Mass spectrum of CEESO. The mass spectrum was tested after catalytic reaction of CEES.

9. $^1\text{H-NMR}$ Spectra of CEES Oxidation Process with V-Co-MOF as Catalyst.

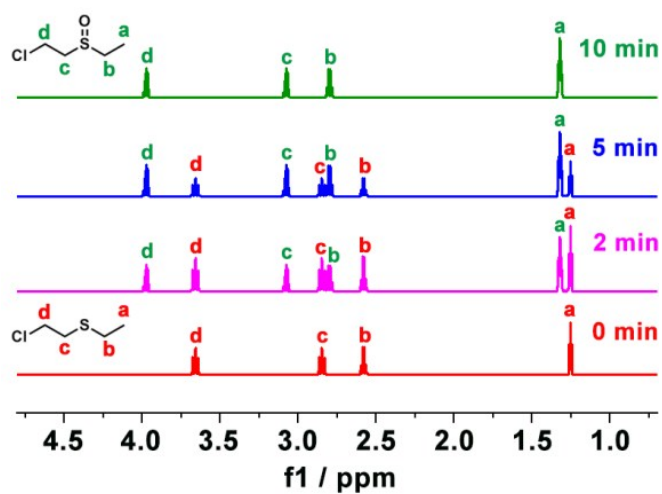


Figure S7. $^1\text{H-NMR}$ spectra of CEES oxidation process with V-Co-MOF as catalyst. Reaction condition: CEES (0.25 mmol), 30% H_2O_2 (0.30mmol), V-Co-MOF (0.025mmol), and EtOH (2.0 mL) at 25 $^\circ\text{C}$ for 10 min and analyzed by $^1\text{H-NMR}$ (CDCl_3).

10. The influence of the Quantity of Catalyst and Oxidant for CEES Oxidation.

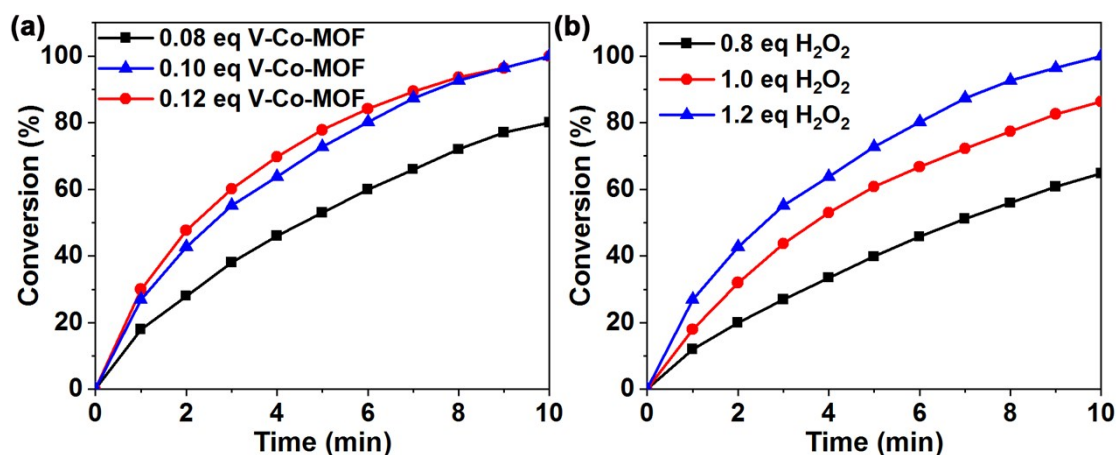


Figure S8. (a) The influence of catalyst amount for the oxidation of CEES with V-Co-MOF as catalyst. (b) The influence of oxidant amount for the oxidation of CEES with V-Co-MOF as catalyst.

11. Kinetic Analysis of CEES Oxidation for V-Co-MOF and V-Ni-MOF

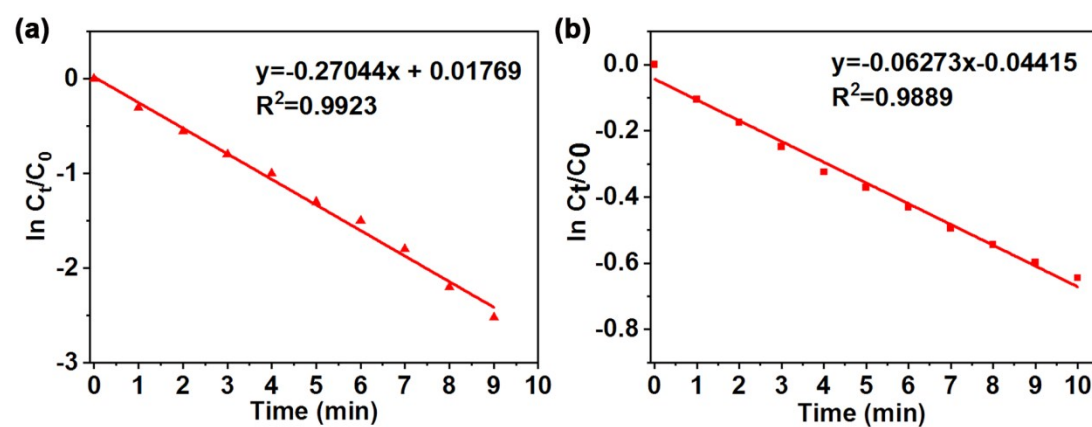


Figure S9. The kinetic analysis of CEES oxidation for V-Co-MOF (a) and V-Ni-MOF (b) ($\ln(C_t/C_0)$ versus reaction time).

12. PXRD Patterns of NaK{V₂O₆}

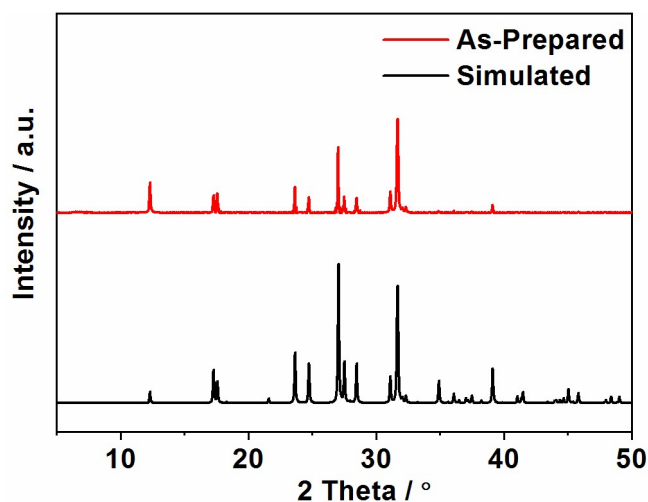


Figure S10. The PXRD patterns of NaK{V₂O₆}.

13. FTIR Spectra of CEES Molecules Absorbed on V-Co-MOF and V-Ni-MOF

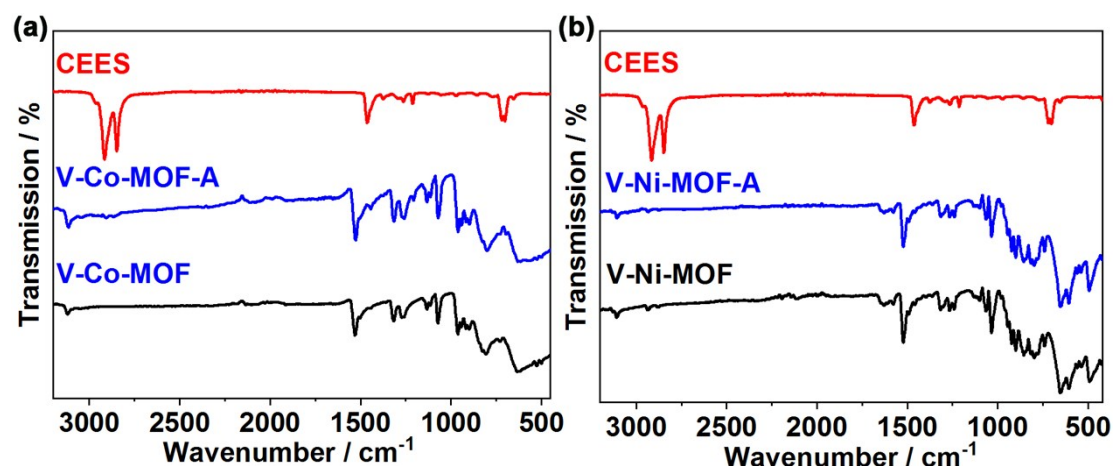


Figure S11. The FTIR spectra of V-Co-MOF (a) and V-Ni-MOF (b) before and after absorbing CEES, and the FTIR spectrum of CEES. Note: A = After absorbing CEES.

The treatment procedure of the samples (V-Co-MOF-A and V-Ni-MOF-A) before testing FTIR spectra: CEES (0.25 mmol), V-Co-MOF or V-Ni-MOF (0.025 mmol) and EtOH (2 mL) were placed in 10mL sealed vial and stirred at 25 °C for 60 min. Then we removed the external CEES by centrifugation and the obtained solids were washed with fresh EtOH. Finally the solids were dried at room temperature and named as V-Co-MOF-A or V-Ni-MOF-A.

14. XPS Spectra of Co^{2+} in V-Co-MOF-A and Ni^{2+} in V-Ni-MOF-A

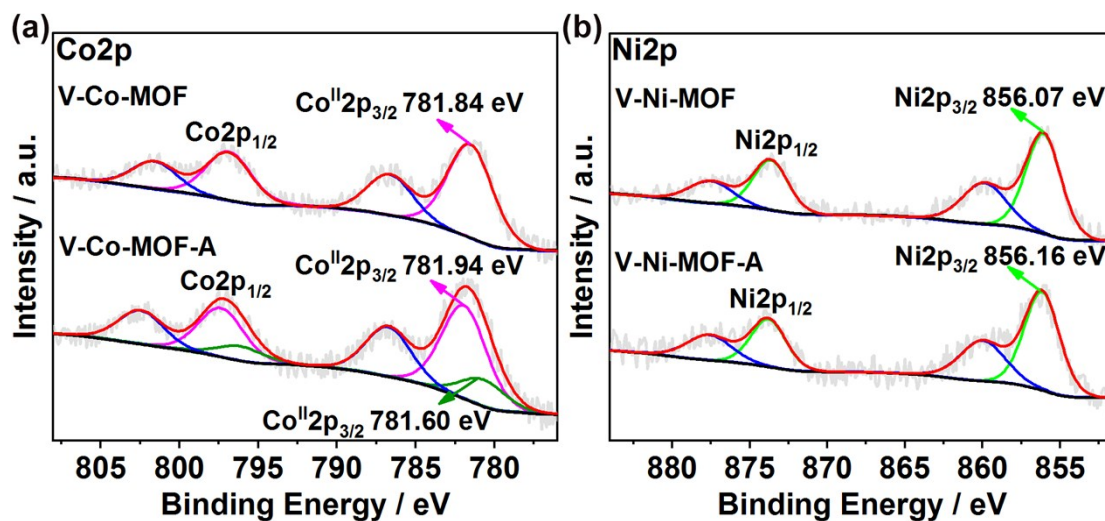


Figure S12. XPS spectra of Co^{2+} in V-Co-MOF-A (a) and Ni^{2+} in V-Ni-MOF-A (b).

Note: A = After absorbing CEES.

15. FTIR Spectra and Raman Spectra of V-Co-MOF-treating with 30% H_2O_2

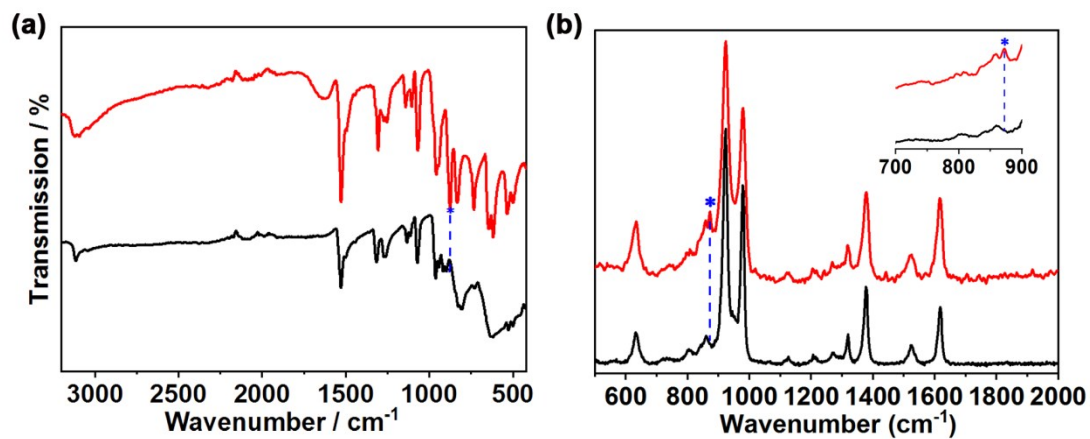


Figure S13. (a) FTIR spectra of V-Co-MOF before (black line) and after (red line)

treating with 30% H_2O_2 . (b) Raman spectra of V-Co-MOF before (black line) and

after (red line) treating with 30% H_2O_2 .

16. Comparison of CEES Catalytic Oxidation by Different Catalysts

Table S3. Comparison of CEES catalytic oxidation by different POVs and POMOFs catalysts.

Entry	Catalyst	Time (min)	Oxidant	T (°C)	Conv.(%)	Sulfoxide selectivity (%)	Refs.
1	V-Co-MOF	10	H ₂ O ₂	25	100	100	This work
2	V-Ni-MOF	10	H ₂ O ₂	25	47.5	100	This work
3	PNb ₁₂ V ^V V ₄ ^{IV}	60	H ₂ O ₂	25	100	67	[1]
4	V ₆ O ₁₁ (OMe) ₈	240	H ₂ O ₂	25	100	85	[2]
5	TBA-polyV ₆	30	H ₂ O ₂	25	99	100	[3]
6	H ₅ PV ₂ Mo ₁₀ O ₄₀ @MIL-101	120	O ₂	25	97.4	100	[4]
7	PW ₁₂ @NU-1000	20	H ₂ O ₂	45	98	57	[5]
8	PW ₁₂ @NU-1000-scCO ₂	5	H ₂ O ₂	45	100	90	[6]
9	PV ₂ Mo ₁₀ @ NU-1000	45	O ₂	70	100	<100	[7]

17. References

- 1 J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang, C. L. Hill and C. Hu, *Angew. Chem. Int. Ed.*, 2017, **56**, 4473-4477.
- 2 J.-K. Li, J. Dong, C.-P. Wei, S. Yang, Y.-N. Chi, Y.-Q. Xu and C.-W. Hu, *Inorg. Chem.*, 2017, **56**, 5748-5756.
- 3 K. P. Sullivan, W. A. Neiwert, H. Zeng, A. K. Mehta, Q. Yin, D. A. Hillesheim, S. Vivek, P. Yin, D. L. Collins-Wildman, E. R. Weeks, T. Liu and C. L. Hill, *Chem. Commun.*, 2017, **53**, 11480-11483.
- 4 Y. Li, Q. Gao, L. Zhang, Y. Zhou, Y. Zhong, Y. Ying, M. Zhang, C. Huang and Y. a. Wang, *Dalton Trans.*, 2018, **47**, 6394-6403.
- 5 C. T. Buru, P. Li, B. L. Mehdi, A. Dohnalkova, A. E. Platero-Prats, N. D. Browning, K. W. Chapman, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 5174-5181.
- 6 C. T. Buru, A. E. Platero-Prats, D. G. Chica, M. G. Kanatzidis, K. W. Chapman and O. K. Farha, *J. Mater. Chem. A*, 2018, **6**, 7389-7394.
- 7 C. T. Buru, M. C. Wasson and O. K. Farha, *ACS Appl. Nano Mater.*, 2019, **3**, 658-664.