Supplementary Materials

Importance of surface peroxo species in the epoxidation of cyclohexene by Mo-doped TS-1 and O_2 under solvent-free conditions

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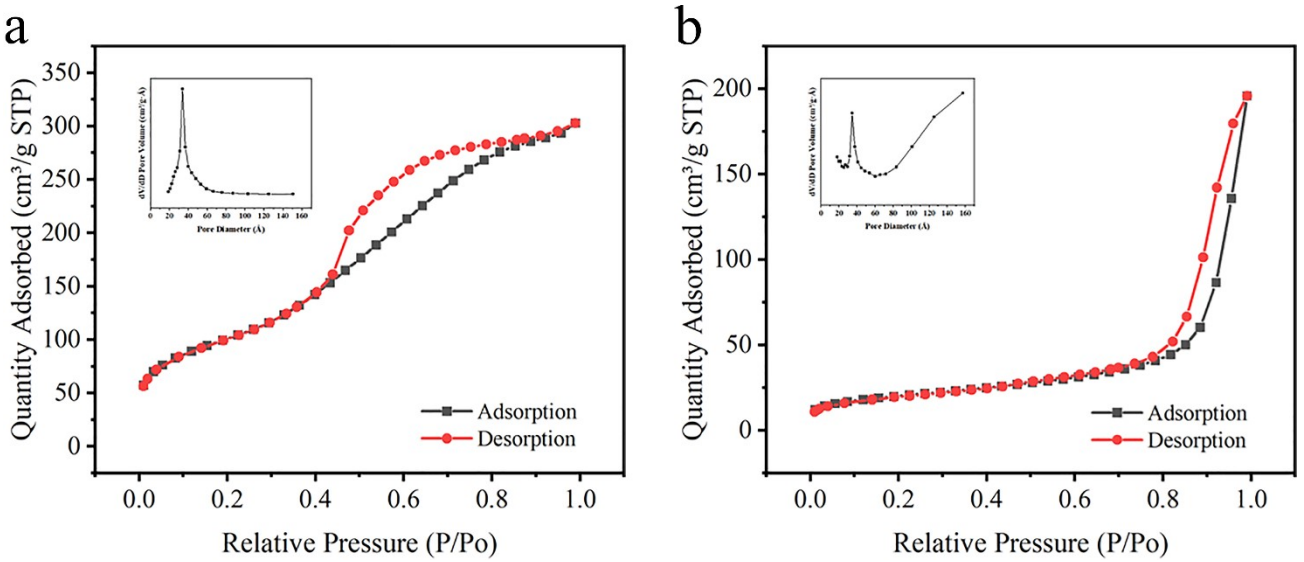

Figure S1. N_2 adsorption/desorption isotherm inserted with pore size distributions of (a) TS-1, (b)5Mo-TS-1.

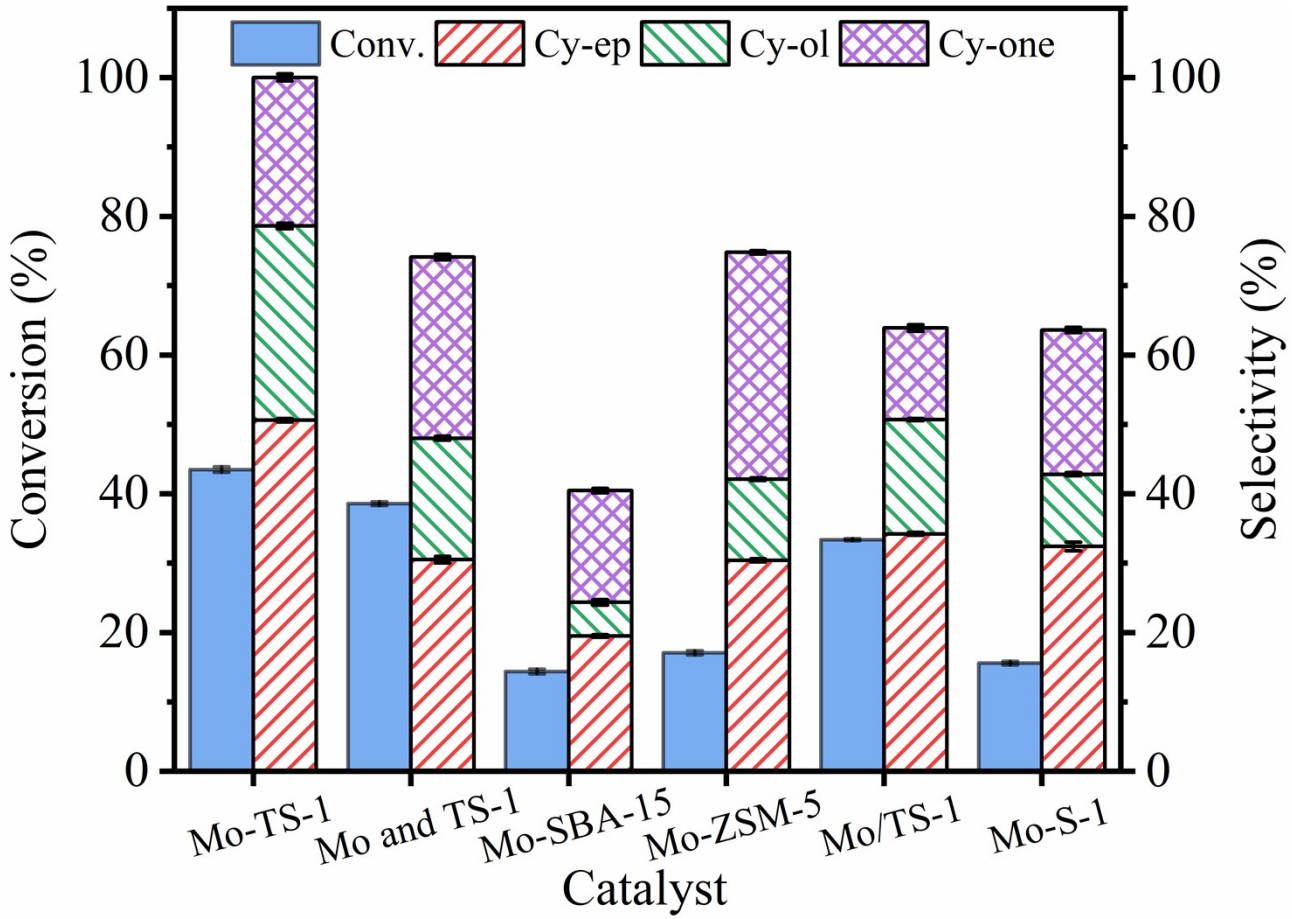

Figure S2. Oxidation of Cy by various catalysts and O_2. Reaction conditions: 50 mg of catalyst, 5 mL of Cy, 1.0 MPa O_2, 80 °C and 6 h reaction time. Mo and TS-1: 1.0 wt.% Mo physical mixing with 99.0 wt.% TS-1, Mo/TS-1:

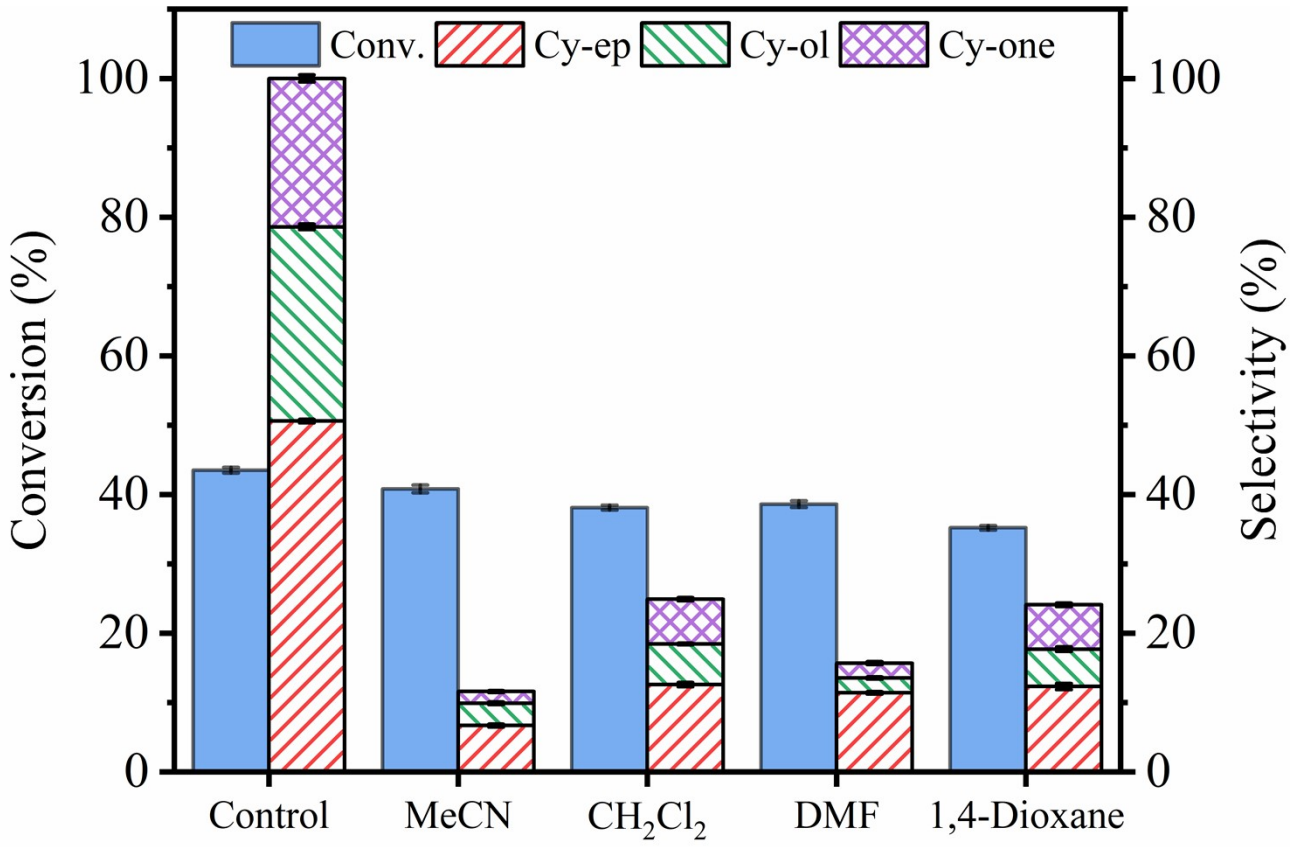

Figure S3. Oxidation of Cy in various solvents by 5Mo-TS-1 and O_2. Reaction conditions: 50 mg of catalyst, 5 mL of Cy, 1.0 MPa O2, 80 °C and 6 h reaction time.

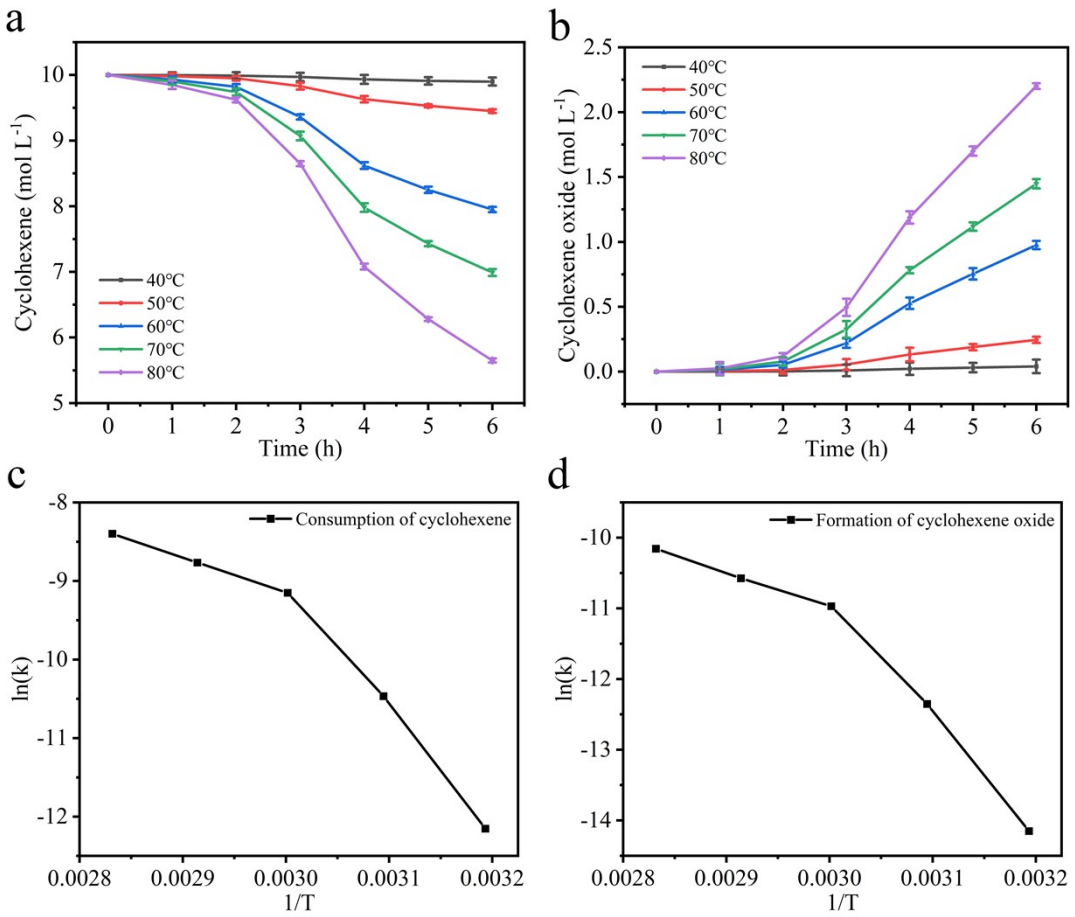

Figure S4. (a) The total consumption of Cy and (b) the formation of Cy-ep in the various temperatures. Arrhenius plots of ln (initial rate) versus 1/T in (c) consumption of Cy and (d) formation of Cy-ep.

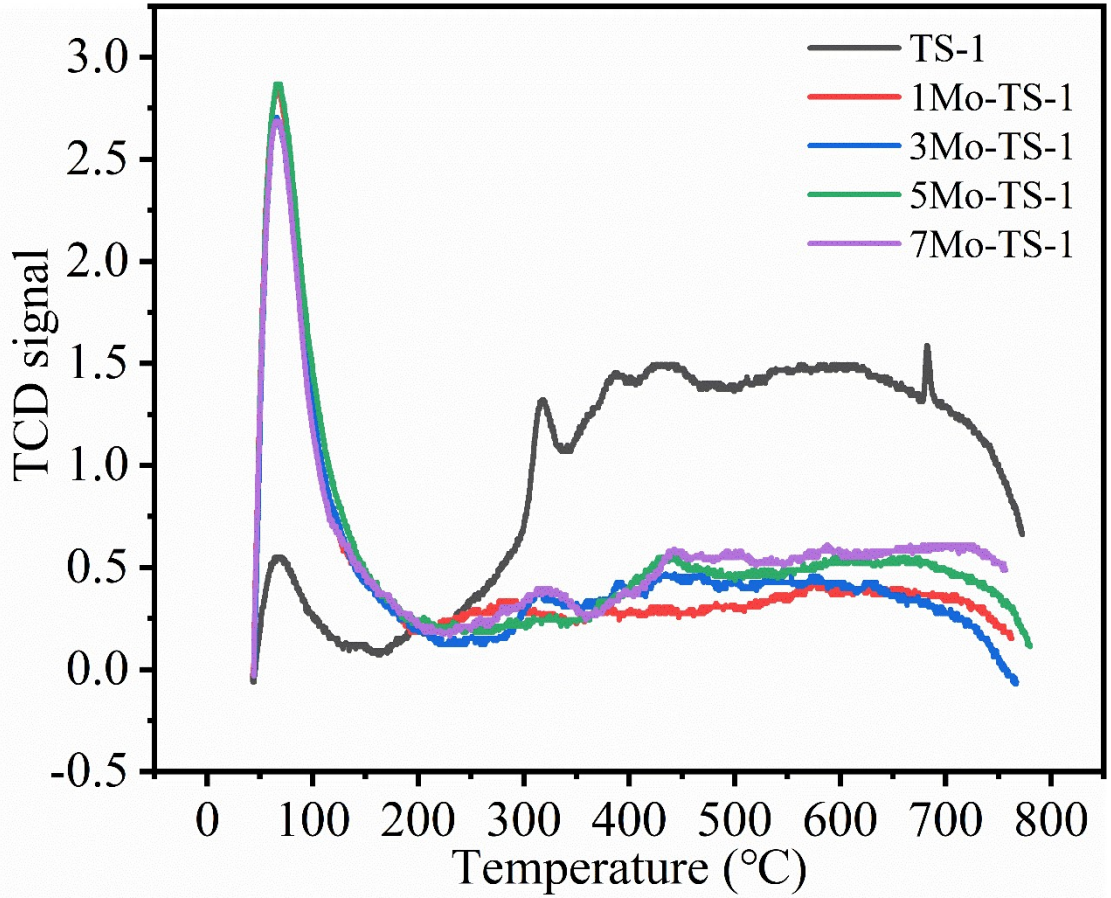

Figure S5. H_2-TPR profiles of various catalysts.

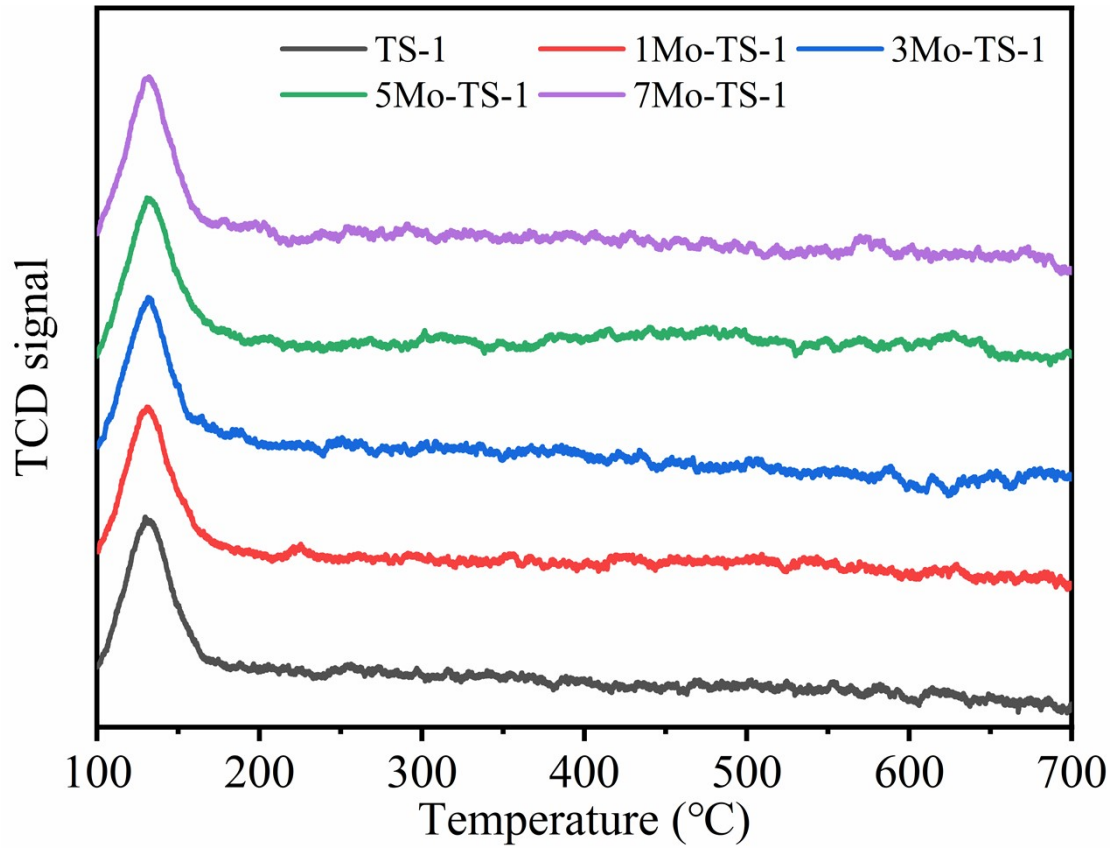

Figure S6. NH_3-TPD profiles of various catalysts

Table S1. BET surface areas of TS-1 and 5Mo-TS-1

Samples	S_{BET} (m^2 g^{-1})	Average pore diameter (nm)
TS-1	363	5.16
5Mo-TS-1	60	17.00

Table S2. ICP-OES analysis of different catalysts and reaction mixture.

Samples	Mo percentage (wt.%)[a]	Ti percentage (wt.%)[a]
5Mo-TS-1	1.08	1.22
Reused 5Mo-TS-1	1.09	1.24
Reaction mixture	-[b]	-[b]

[a] the amounts of Mo and Ti in the catalyst before and after reaction

[b] no detection by ICP-OES

Table S3. Mulliken charges, spin populations and bond lengths of various species during O_2 activation

	Mulliken charge (*e*) /spin				Bond length (Å)
	O^1	O^2	Ti	Mo	O^1-O^2
O_v-O_2	-0.36/0.53	-0.47/0.50	1.38/0.18	1.18/1.70	1.394
Mo site-O_2 R	0/0	0/0	1.55/0	1.54/0	1.248
Mo site-O_2 TS	-0.06/0	-0.02/0	1.6/0	1.6/0	1.254
Mo site-O_2 P	-0.37/0	-0.30/0	1.67/0	1.95/0	1.461

Table S4. Mulliken charges, spin and bond lengths of various species during the abstraction of allyl H and vinylic H by Mo-TS-1 and O_2

	Mulliken charge (*e*) /spin								Bond length (Å)	
	O^1	O^2	Ti	Mo	C(Cy)	H(Cy)	C_6H_{10}	C_6H_9	O^1-O^2	C-H
O_v-superoxo-allylic H R	-0.36/0.53	-0.47/0.50	1.38/0.18	1.18/1.70	-0.51/0	0.22/0	-0.19/0	-0.41/0	1.394	1.074
O_v-superoxo-allylic H TS	-0.39/-0.04	-0.46/0.08	1.44/0.21	1.21/1.45	-0.44/0.01	0.25/-0.01	0.27/0.11	0.02/0.12	1.430	1.318
O_v-superoxo-allylic H P	-0.06/0	-0.04/0	1.36/0.23	1.13/0.86	-0.09/0.62	0.46/0	0.57/0.98	0.11/0.98	1.489	1.901
Mo-peroxo-allylic H R	-0.37/0	-0.30/0	1.67/0	1.95/0	-0.51/0	0.22/0	-0.19/0	-0.41/0	1.461	1.074
Mo-peroxo-allylic H TS	-0.51/0	-0.47/0	1.76/0	2.00/0	-0.44/0	0.25/0.02	0.35/0.71	0.1/0.41	2.087	1.233
Mo-peroxo-allylic H P	-0.82/0	-0.6/0	1.77/0	1.97/0	-0.07/0.57	0.4/0	1.08/0.97	0.68/0.97	2.628	2.975
Mo-peroxo-vinylic H R	-0.37/0	-0.30/0	1.67/0	1.95/0	-0.19/0	0.11/0	-0.19/0	-0.3/0	1.461	1.074
Mo-peroxo-vinylic H TS	-0.49/0	-0.5/0	1.77/0	2/0	-0.1/0.21	0.2/0	0.42/0.69	0.22/0.69	2.193	1.088
Mo-peroxo-vinylic H P	-0.57/0	-0.74/0	1.81/0	2.01/0	0.12/0.57	0.41/0	0.49/0.97	0.08/0.97	2.502	2.228

Table S5. Mulliken charges, spin populations and bond lengths of various species during C=C oxidation by Mo-peroxo of Mo-TS-1

	Mulliken charge (*e*) /spin					Bond length (Å)					
	O^1	O^2	Ti	Mo	C_6H_{10}	O^1-O^2	C^1=C^2	Mo-O^1	Mo-O^2	C^1-O^2	C^2-O^2
Mo-peroxo-C=C R	-0.37/0	-0.30/0	1.67/0	1.95/0	-0.18/0	1.461	1.339	2.047	2.082	3.073	2.913
Mo-peroxo-C=C TS	-0.56/0	-0.48/0	1.77/0	1.94/0	0.5/0	2.109	1.364	1.904	2.175	2.842	2.672
Mo-peroxo-C=C P	-0.56/0	-0.5/0	1.74/0	1.98/0	0.44/0	2.658	1.451	1.771	3.082	1.496	1.495

Entry	Catalyst	Reaction condition	Cyclohexene conversion (%)	Cyclohexene oxide selectivity (%)
1	MoO_3[1]	50 mg catalyst, 5 mmol cyclohexene, 80 ℃, 0.6 ml TBHP, 2 h, 2 ml toluene	14.8	23.6
2	$PVAD_1$-PMo[2]	100 mg catalyst, 130 ℃, 0.6 MPa O_2, 6 h	65.3	25.0
3	MIL-88A(Fe)[3]	50 mg catalyst, 9.85 mmol cyclohexene, 3.0 mL solvent, 80 ℃, 8 h, 0.5 MPa O_2	81.4	11.3
4	PS-DA-Co[4]	2 mg catalyst, 9.85 mmol cyclohexene, 3.0 mL solvent, 70 ℃, 10 h, 0.1 MPa O_2	22.2	12.5
5	V_2O_5-MoO_3@SiO_2[5]	10 mg catalyst, 5 mmol cyclohexene, 7.5 mmol H_2O_2, 10 mL acetonitrile, 55 ℃, 10h	67.0	21.0
6	VOTMCPP@N-SBA[6]	30 mg catalyst, 1 mL cyclohexene, 3 mL H_2O_2, 5 mL acetonitrile, 25 ℃, 4h	85.0	3.0
7	FeO_x/NCNT[7]	50 mg catalyst, 8.0 g cyclohexene, 9.6g acetonitrile, 80 ℃, 10 h, 1 MPa O_2, 2.5 g *o*-DCB	53.2	3.9
8	NH_4F_MTS-1[8]	100 mg catalyst, 20 mmol cyclohexene, 10 mL acetonitrile, 70 ℃, 5 h, 20mmol H_2O_2	27.1	28.0
9	MoO_3@np-Au[9]	10 mg catalyst, 15 mL cyclohexene, 0.5 mL undecane (internal standard), 0.27 mL *tert*-butyl hydroperoxide, 0.4 MPa O_2, 90 ℃, 4 h	3.5	73.1
10	Mg-Mo bimetallic oxide[10]	50 mg catalyst, 5 mL cyclohexene, 1 MPa O_2, 80℃, 8 h	31.0	49.3
11	Mo@N:C[11]	10 mg catalyst, 2.5 mL cyclohexene, 15 mL acetonitrile, 1 MPa O_2, 70℃, 16 h, 0.5 mL (1.85 mmol) cyclohexane (IS)	45.0	5.0
12	This work	50 mg catalyst, 5 mL cyclohexene, 1 MPa O_2, 80℃, 8 h	43.5	50.6

Table S6. Various Processes for the Epoxidation of Cyclohexene.

Reference

1. P. Sudarsanam, N. Singh and P. N. Kalbande, *Catal Commun*, 2022, **164**, 106433.
2. Y. Wu, M. Su, Y. Xiao, B. Guang and Y. Liu, *Ind Eng Chem Res*, 2021, **61**, 299-306.
3. N. Li, C. Jian, Y. Song, L. Wang, A. U. Rehman, Y. Fu, F. Zhang, D.-L. Chen and W. Zhu, *Molecular Catalysis*, 2023, **535**.
4. Y. Chang, Y. Lv, F. Lu, F. Zha and Z. Lei, *Journal of Molecular Catalysis A: Chemical*, 2010, **320**, 56-61.
5. G. Yang, M. D. Huff, H. Du, Z. Zhang and Y. Lei, *Catal Commun*, 2017, **99**, 43-48.
6. S. Farahmand and M. Ghiaci, *Microporous and Mesoporous Materials*, 2019, **288**, 109560.
7. Y. Cao, H. Yu, F. Peng and H. Wang, *ACS Catal.*, 2014, **4**, 1617-1625.
8. S.-K. Kim, B. M. Reddy and S.-E. Park, *Ind. Eng. Chem. Res.*, 2018, **57**, 3567-3574.
9. J. Dou and F. Tao, *Applied Catalysis A: General*, 2017, **529**, 134-142.
10. Y.-Z. Xu, Y.-L. Wang, Y.-D. Shan, S.-H. Wu, Y. Liu and X. Han, *Ind Eng Chem Res*, 2024, **63**, 14554-14566.
11. I. M. Denekamp, M. Antens, T. K. Slot and G. Rothenberg, *ChemCatChem*, 2018, **10**, 1035-1041.