Supporting Information

Insights into the effect of oxygen vacancy on epoxidation of 1-hexene with hydrogen peroxide over WO_{3-x}/SBA-15

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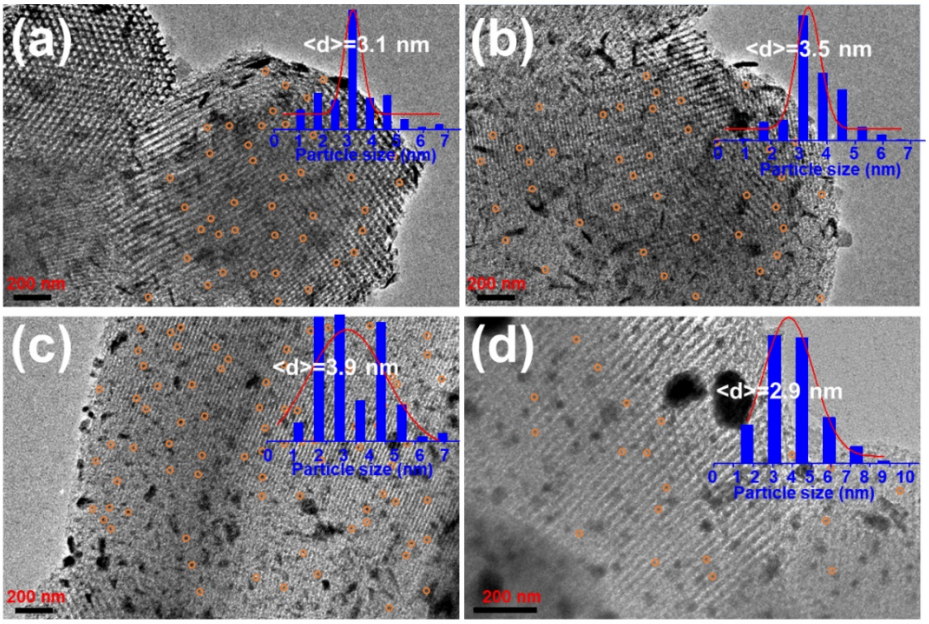

Fig. S1. TEM images of the WO_{3-x}/SBA-15 catalysts, H300-W (a), H400-W (b), H600-W (c) and H700-W (d).

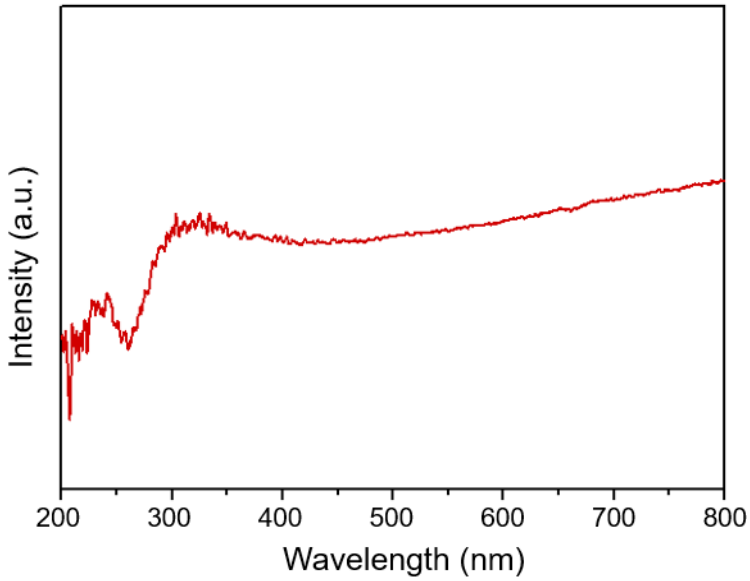

Fig. S2. UV-vis spectrum of bare SBA-15.

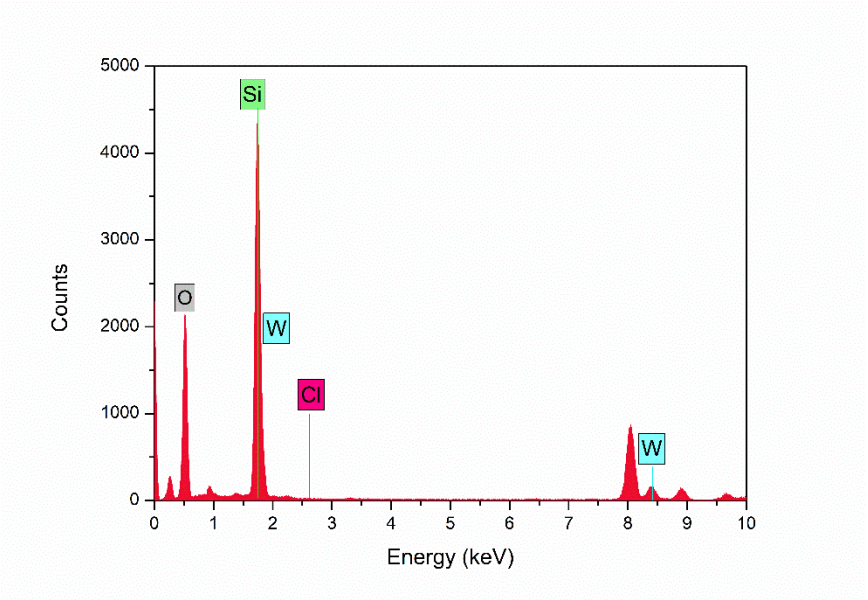

Fig. S3. EDS spectrum of elementary of H500-W.

Table S1. Elementary analysis results of H500-W.

El	AN	Series	unn. (wt.%)	norm. (wt.%)	Atom. (at.%)	Error (1 Sigma) (wt.%)
Si	14	K-series	46.67	46.67	40.70	0.2
O	8	K-series	37.32	37.32	57.15	1.16
W	74	L-series	15.98	15.98	2.13	1.64
Cl	17	K-series	0.03	0.03	0.02	0.03

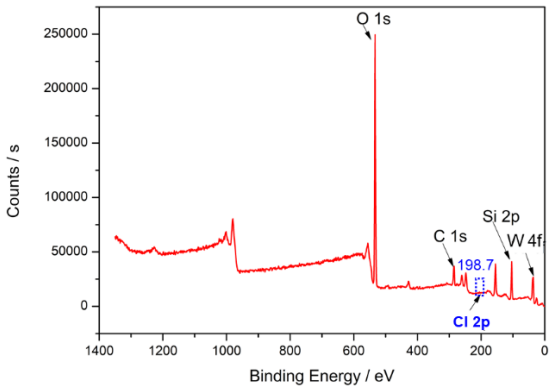

Fig. S4. XPS survey of H500-W.

Table S2. The comparison of W-based heterogenous catalysts for terminal liner olefins.

Catalyst	Solvent	Substrate	Oxidant [a]	n(substrate): $n(H_2O_2)$	Temp. (°C)	Time (h)	TOF (h^{-1})	Select. (%)	Ref
H500-W	CH_3CN	1-hexene	H_2O_2	1:1	70	1.5	2.2	70.2	This work
W-Zn/SnO_2	DMC	1-hexene	H_2O_2 (60 wt%)	5:1	60	4	6.9	89	1
WO_x/C	CH_3CN	1-hexene	H_2O_2	1:1	60	10	0.8	89.2	2
W-BEA	CH_3CN	1-hexene	H_2O_2 (32.6%)	10:1	40	N.A.	1.8	N.A.	3
Ag-W [b]	CH_3CN	1-hexene	H_2O_2 (50 wt%)	1:3	RT	18	11.1	99	4
W-KIT-6	MeOH	ethylene	H_2O_2	--	35	5	1.8	80	5
MWCNTs	CH_3CN	heptene	H_2O_2	1:5	77	3	5.6	100	6

TOF=n(epoxide)/(n(metal W)·t(reaction time)); [a] H_2O_2 with 30 wt%. [b] TOF is calculated based on the mole of Ag.

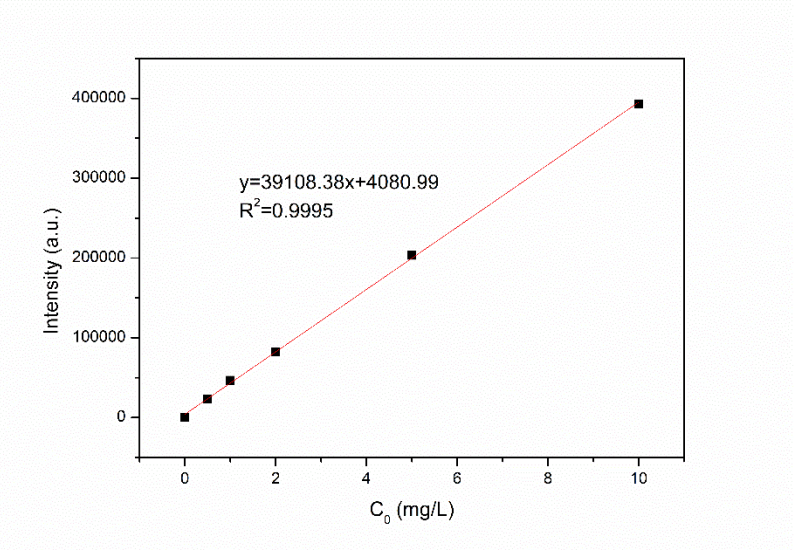

Fig. S5. Calibration curves for ICP-OES measurement.

Table S3. The content of metallic W in WO_{3-x}/SBA-15 catalysts measured by ICP-OES. [a]

Entry	Catalyst	m [c] (g)	V_0 [d] (mL)	C_0 [e] (mg/L)	f [f]	C_x [g] (mg/kg)	w (%)	Ave. w(%)	Error
1	H300-W	0.0563	25	2.076	100	92184.7	9.22		
1	H300-W	0.0563	25	2.081	100	92406.7	9.24	9.23	0.11%
2	H400-W	0.0503	25	1.777	100	88320.1	8.83		
2	H400-W	0.0503	25	1.785	100	88717.7	8.87	8.85	0.23%
3	H500-W	0.0717	25	2.611	100	91039.1	9.10		
3	H500-W	0.0717	25	2.621	100	91387.7	9.14	9.12	0.22%
4 [b]	H500-W	0.0468	25	1.672	100	89316.2	8.93		
4 [b]	H500-W	0.0468	25	1.684	100	89957.3	9.0	8.97	0.45%
5	H600-W	0.0774	25	2.809	100	90730.0	9.07		
5	H600-W	0.0774	25	2.813	100	90859.2	9.09	9.08	0.11%

[a] The metal content was calculated by the definitions: $C_x(mg/kg)=(C_0(mg/L)\cdot f\cdot V_0(mL)\cdot 10^{-3})/(m(g)\cdot 10^{-3})$ (1), $w(\%)=(C_x(mg/kg)\cdot 100\%)/10^6$ (2). [b] The oxidative H500-W catalyst was prepared by calcining the as-prepared H500-W catalyst at 500 °C under flowing oxygen (5 vol%) for 2 h. [c] m(g) represents the mass of the catalyst used. [d] V_0(mL) represents the volume after sample dissolution. [e] C_0(mg/L) represents the metal concentrations of the tested solution which obtained by the instrument. [f] f represents the dilution factor. [g] C_x(mg/kg) represents the metal content in the test solution.

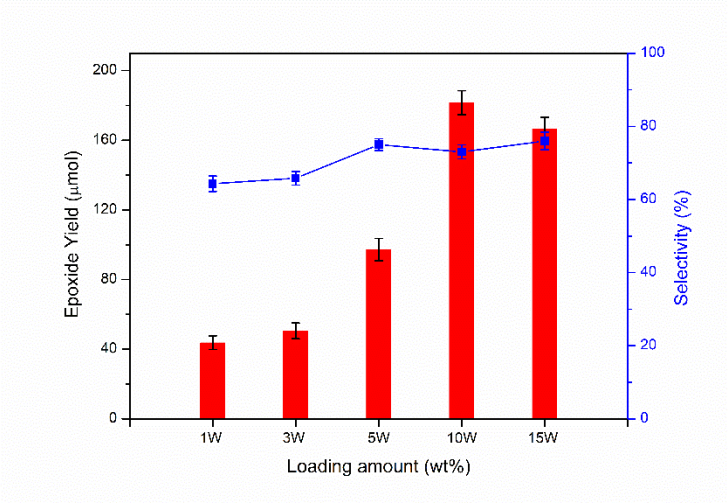

Fig. S6. The influence of WO_{3-x} loading content on the epoxidation of 1-hexene with H_2O_2. The catalysts with different loading amounts were all reduced at 500 °C and the loading amounts are 1 wt%, 3 wt%, 5 wt%, 10 wt% and 15 wt%, respectively. Reaction conditions: 75 mg of catalyst, 4 mmol of 1-hexene, 4 mmol of H_2O_2 (30 wt%), 10 mL of CH_3CN, 70 °C and reaction for 3 h.

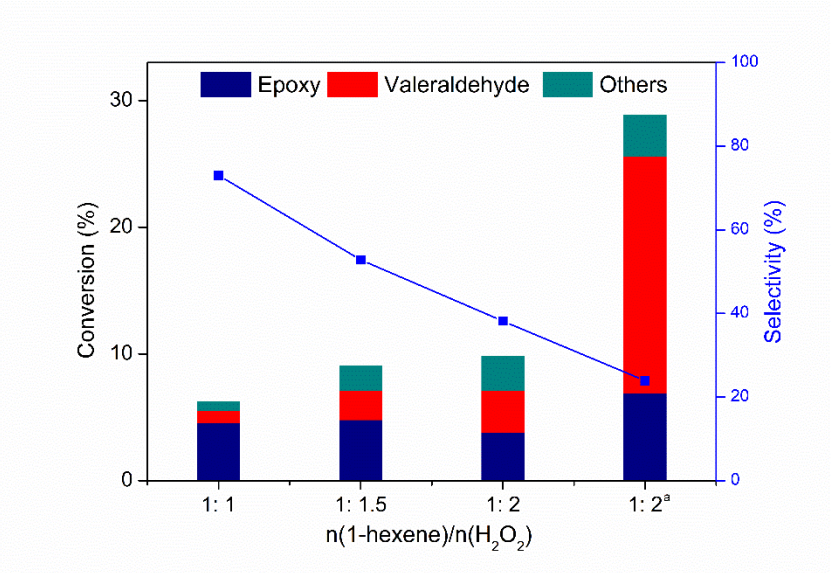

Fig. S7. The influence of molar ratio of n(1-hexene)/n(H_2O_2) on the epoxidation of 1-hexene with H_2O_2. Reaction conditions: 75 mg of catalyst (H500-W), 4 mmol of 1-hexene, the specified amount of H_2O_2 (30 wt%), 10 mL of CH_3CN, 70 °C and reaction for 3 h. [a] 100 mg of catalyst (H500-W), reaction for 18 h.

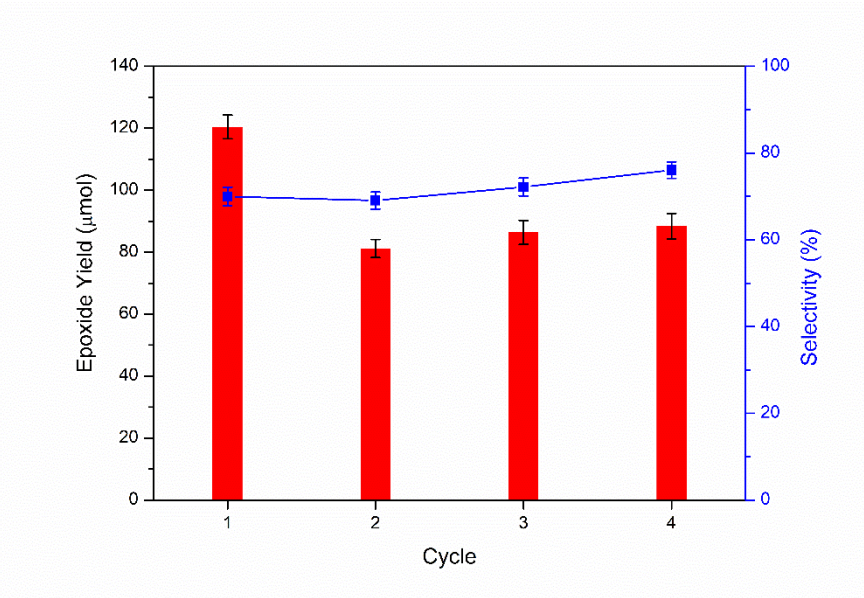

Fig. S8. Recycling tests of 1-hexene epoxidation over H500-W catalyst. Reaction conditions: 75 mg of catalyst, 4 mmol of 1-hexene, 4 mmol of H_2O_2 (30 wt%), 10 mL of CH_3CN, 70 °C and reaction for 1.5 h.

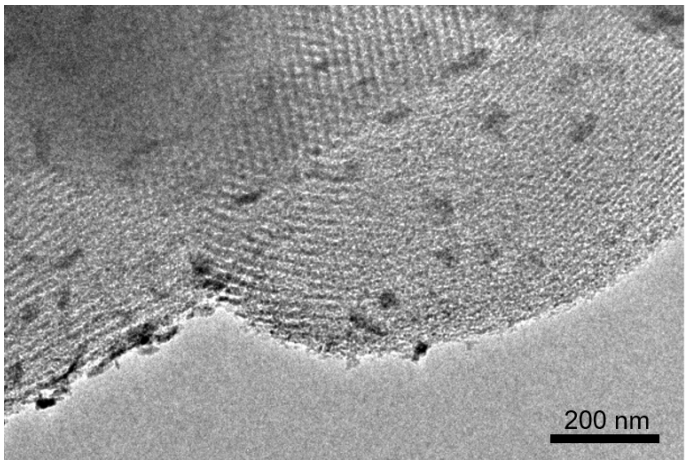

Fig. S9. TEM image of used H500-W catalyst.

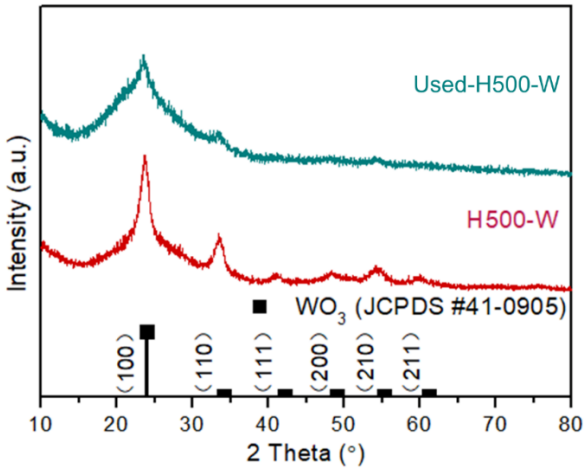

Fig. S10. XRD patterns of wide-angle of used H500-W (dark cyan) and fresh H500-W catalysts (red).

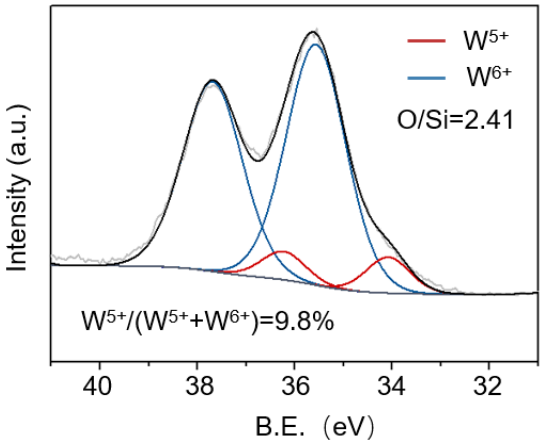

Fig. S11. XPS W 4f binding energy spectra of used H500-W catalyst.

TEM image of the recovered catalyst after the fourth run displayed less WO_{3-x} nanoparticles, but the distribution and morphology of WO_{3-x} nanoparticles didn't change (Fig. S9). The recovered catalyst performed the similar diffraction peaks (Fig. S10) and surface electronic structure (Fig. S11) to those of the fresh catalyst, indicating that almost no damage to oxygen vacancy.

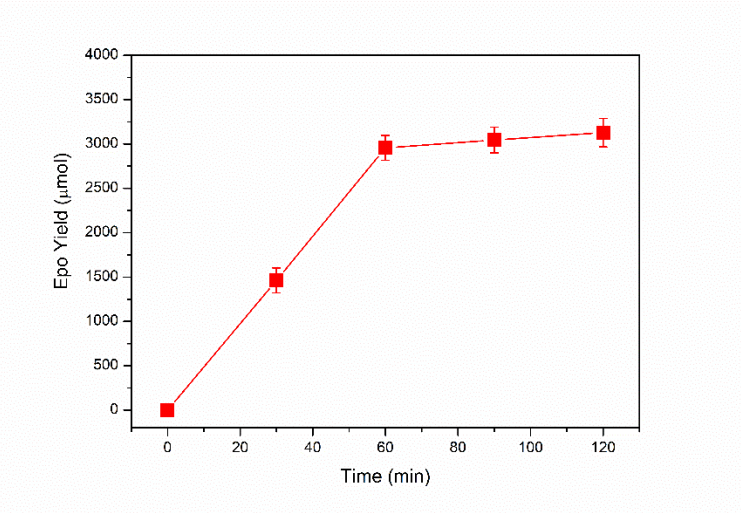

Fig. S12. The hot filtration experiment of cyclooctene epoxidation on H500-W catalyst. Reaction conditions: 75 mg of catalyst (H500-W), 4 mmol of 1-hexene, 4 mmol of H_2O_2 (30 wt%), 10 mL of CH_3CN, 70 °C, and the catalyst was removed after reaction for 60 min.

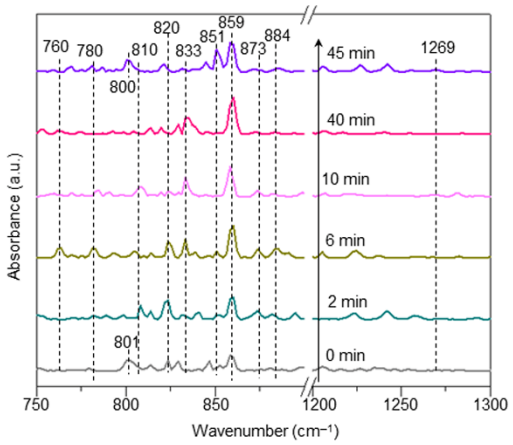

Fig. S13. The profiles of in situ FT-IR spectra of H500-W catalyst at 30 °C

Table S4. The results of in situ FT-IR.

Bands (cm^{-1})	Ascription	Ref.
760	stretching vibrations of O-W-O	*J. Solid State Chem.*, **1987**, 67, 235–247
780	stretching vibrations of O-W-O	*Appl. Catal., B*, **2018**, 221, 169–178
810	H_2O-W vibration	*ACS Catal.*, **2019**, 9, 7641–7650
820	stretching vibrations of W=O	*Mater. Sci. Eng., B*, **2000**, 77, 193–201
833	metal peroxide	*J. Mol. Catal. A: Chem.*, 1996, 114, 169–180; *J. Am. Chem. Soc.,* **2002**, 124, 9292–9298
851	stretching vibrations of O-O	*Catal. Today,* **2000**, 60, 209–218
859	antisymmetric stretching vibration of WO_4^{2-}	P. R. Griffiths, J. A. Haseth, *Fourier Transformation Infrared Spectrometry*, John wiley & Sons, 1986
873	stretching vibration of O–O of H_2O_2	G. Socrates, *Infrared and Raman Characteristic Group Frequencies*, John wiley & Sons, England, 2004
884	stretching vibration of W-O-W	*New J. Chem.,* **2017**, 41, 8520–8529

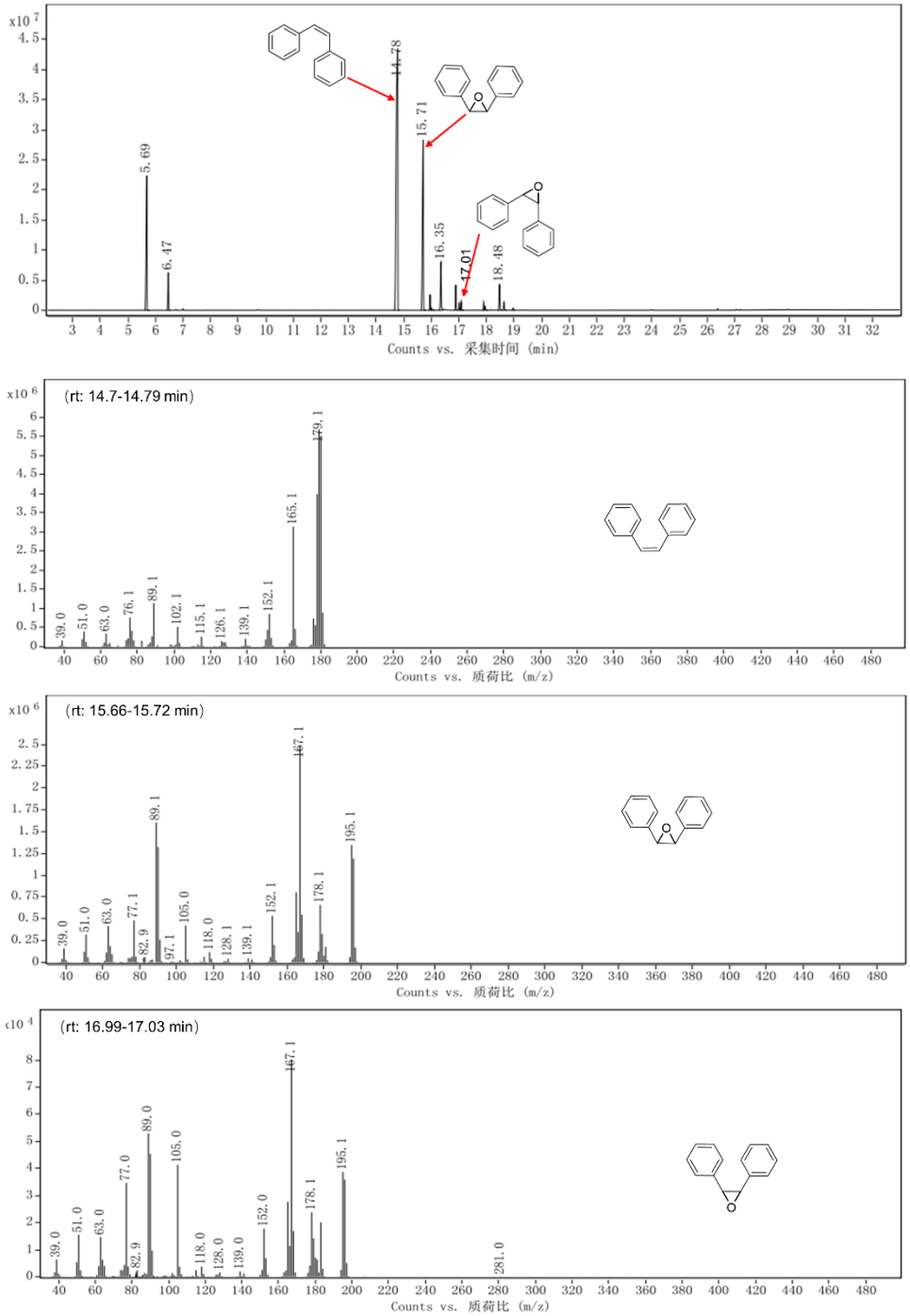

Fig. S14. The results of GC-MS for the epoxidation of cis-stilbene with H_2O_2 over H500-W catalyst.

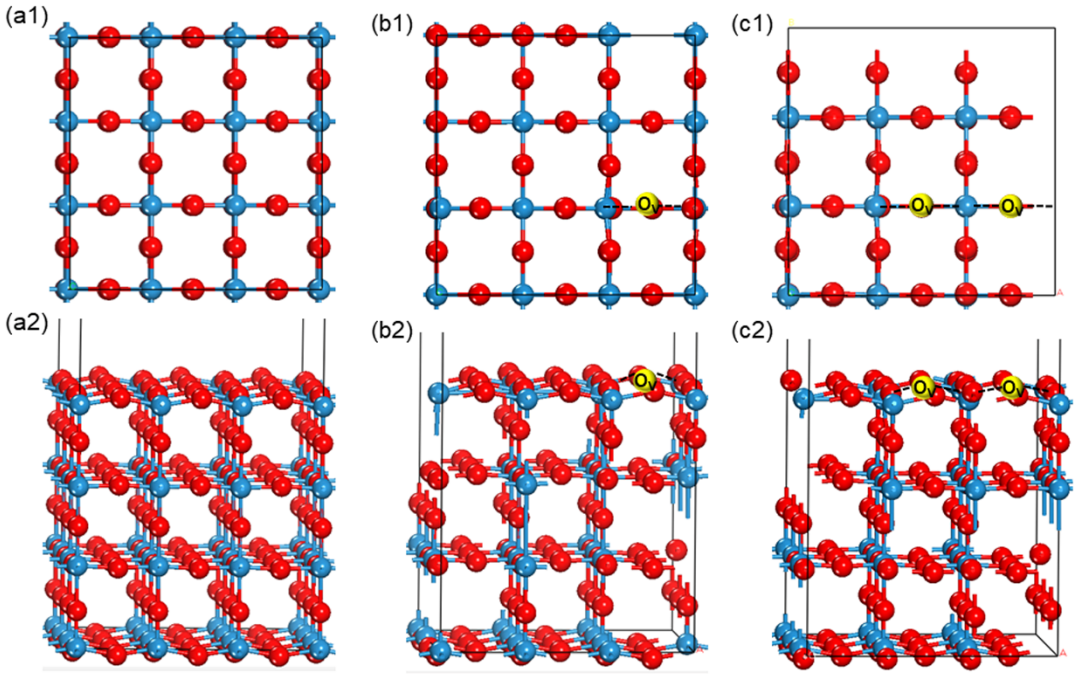

Fig. S15. The optimized structures of WO_3 (100) (a1, a2), WO_3 (100)-1Ov (b1, b2) and WO_3 (100)-2Ov (c1, c2). The blue and red represent W and O atoms, respectively.

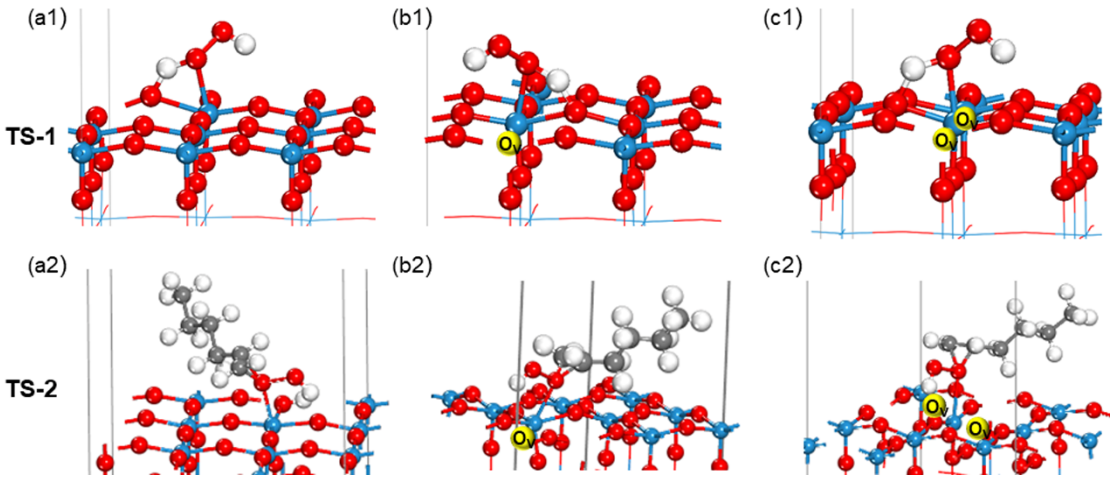

Fig. S16. Optimized structures of the transition state of H_2O_2 dissociation and O transfer on WO_3 (100) (a1,a2), WO_3 (100)-1Ov (b1,b2) and WO_3 (100)-2Ov. The blue, red, white and gray spheres represent W, O, H and C atoms, respectively.

Supplementary references

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