

Supporting Information

Revealing the high activity of WO₃-SBA-15 with isolated tungsten oxide species in cis-cyclooctene epoxidation

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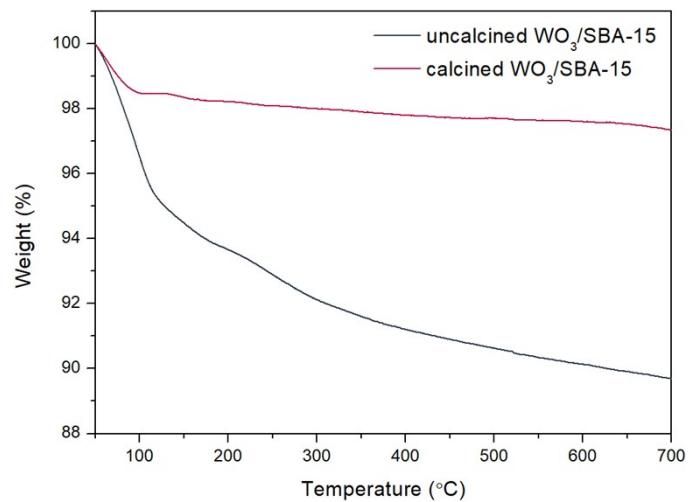


Fig. S1. The thermogravimetric curve of uncalcined WO₃/SBA-15 and calcined WO₃/SBA-15.

TG was conducted on SETSYS EVOLUTION TGA 16/18 (SETARAM Corporation, France). 10 mg of the sample was heated from 25 °C to 800 °C with a heating rate of 10 °C/min in a dynamic air atmosphere. The peroxide tungsten species are not stable enough and could pyrolyze to form tungsten oxide at around 500 °C verified by the TG analysis as reported in the literatures [1-3]. Thus, TG analysis revealed the presence of stable tungsten oxide, but not peroxides, in calcined WO₃/SBA-15.

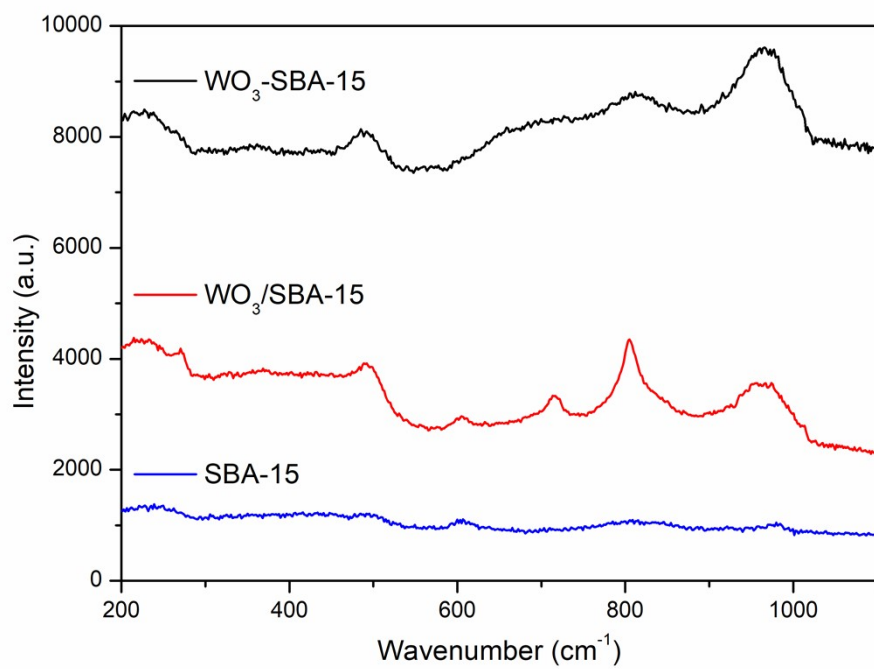


Fig. S2. Raman spectrum of SBA-15. (To illustrate the intensity of peaks assigning to SBA-15, the supported catalysts were also displayed)

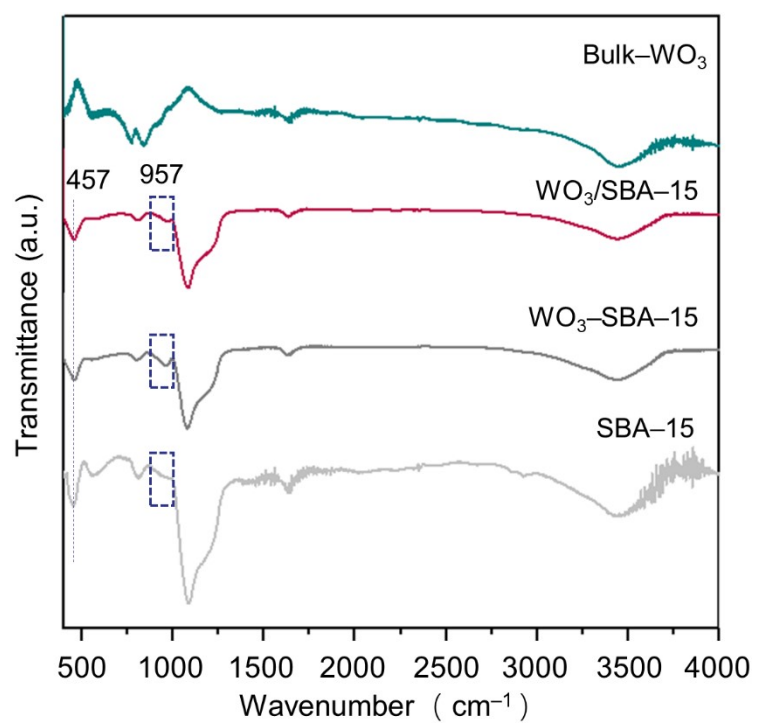


Fig. S3. FT-IR spectra of all samples.

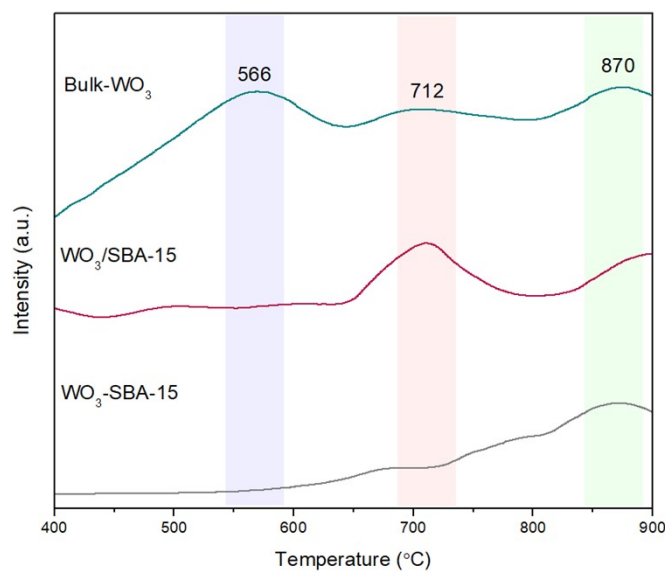


Fig. S4. H₂-TPR profiles of the three catalysts.

H₂-TPR was performed on a Xianquan 5080B apparatus. The as-prepared catalysts (100 mg) were heated at 250 °C for 1 h under an Ar stream (20 mL/min⁻¹). After cooling down to 100 °C, the samples were reduced under a mixture stream of 10 vol% H₂ in Ar (20 mL/min⁻¹) with the temperature ramping rate at 10 °C/min⁻¹. The signal was detected with a thermal conductivity detector (TCD).

Table S1 The equation of standard curve for quantitative analysis.

type	standard curve	Coefficients of determination (R ²)
cis-cyclooctene	$y_1=1.13829x_1-0.00471$	0.99748
cis-cyclooctene oxide	$y_2=1.0982x_2-0.02002$	0.99969

Where, $x_1=\text{Area}(\text{cis-cyclooctene})/\text{Area}(\text{anisole})$, $x_2=\text{Area}(\text{cis-cyclooctene oxide})/\text{Area}(\text{anisole})$, the areas of cis-cyclooctene, cis-cyclooctene oxide and anisole were obtained by the corresponding peak area in gas chromatography results; $y_1=m(\text{cis-cyclooctene})/m(\text{anisole})$, $y_2=m(\text{cis-cyclooctene oxide})/m(\text{anisole})$, the mass of anisole was obtained by weighing. The contents of cis-cyclooctene and cis-cyclooctene oxide can be calculated by bringing these values into the corresponding equations, respectively.

Table S2. Reaction conditions of olefin epoxidation with H₂O₂.

Catalyst	Solvent	Sub.	Oxidant ^a	n(sub.): n(H ₂ O ₂)	Temp. (°C)	Time (h)	Con. (%)	Select. (%)	Ref
W-Zn/SnO ₂	DMC	1-hexene	H ₂ O ₂ (60 wt%)	5:1	60	4	96 ^b	95	[4]
Nb ₂ O ₅ -SiO ₂	MeOH	cyclooctene	H ₂ O ₂ (35 wt%)	2:1	70	5	49	100	[5]
Nb-SiO ₂	MeOH	cyclooctene	H ₂ O ₂	1:1	70	5.	39	100.	[6]
Ag-WO ₃	CH ₃ CN	1-hexene	H ₂ O ₂ (50 wt%)	1:3	80	8	92	95	[7]
H ₂ O-WO _x	CH ₃ CN	cyclooctene	H ₂ O ₂	1:1.175	85	0.75	99.7	98.9	[8]
Ni/SiO ₂ -Liq	CH ₃ CN	cyclohexene	H ₂ O ₂	1:2	90	4	65	74	[9]
Nb/SiO ₂ - Liq	CH ₃ CN	limonene	H ₂ O ₂	1:2	90	3	74	98	[10]
Nb-HAP	CH ₃ CN	limonene	H ₂ O ₂	1:2	90	6	39	62	[11]

^a H₂O₂ with 30 wt%. ^b Con (%) = n(epoxide)/n₀(H₂O₂)*100%.

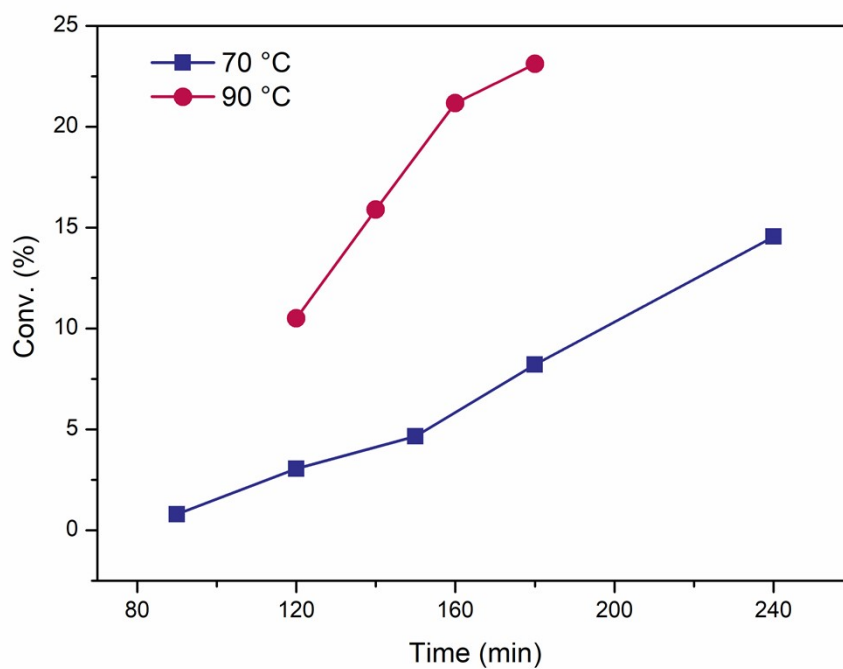


Fig. S5. Profiles of epoxidation of cis-cyclooctene with H_2O_2 over Bulk- WO_3 at different temperatures.

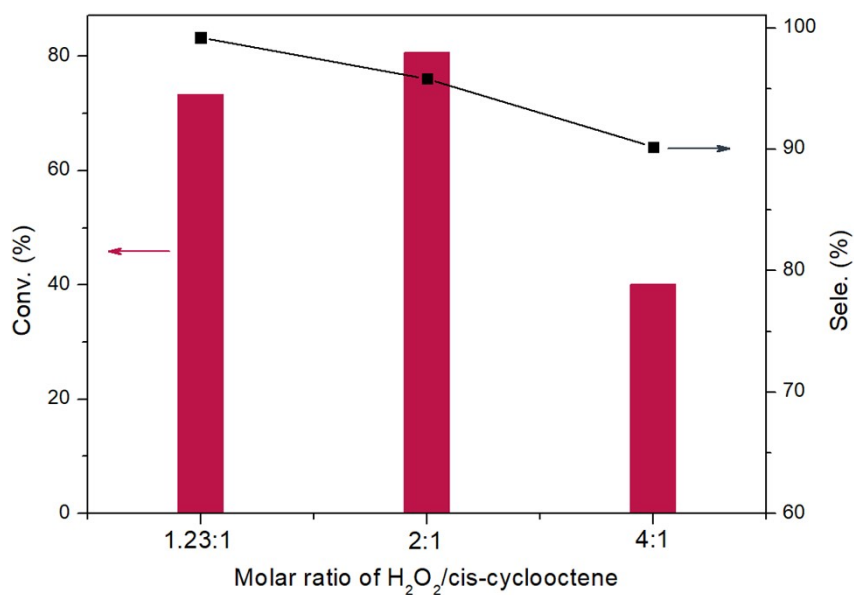


Fig. S6. The catalytic performance of WO₃-SBA-15 with different molar ratio of H₂O₂ to cis-cyclooctene. Reaction conditions: 0.4 mL of cis-cyclooctene, 50 mg of catalyst, 10 mL of acetonitrile, 80 °C and reaction for 1 h.

The decrease of the conversion (with the molar ratio of 4:1) might be due to the formation of an inert layer on the catalyst surface by a large amount of water, which prevented the accessibility of reactant molecules to the active sites [12].

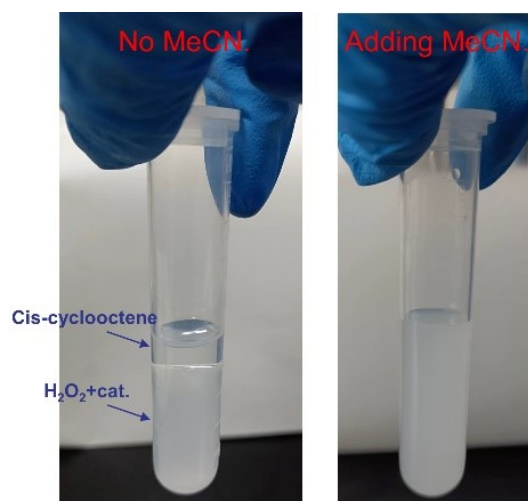


Fig. S7. Mutual solubility of H₂O₂ with cis-cyclooctene in the absence and presence of acetonitrile solvent.

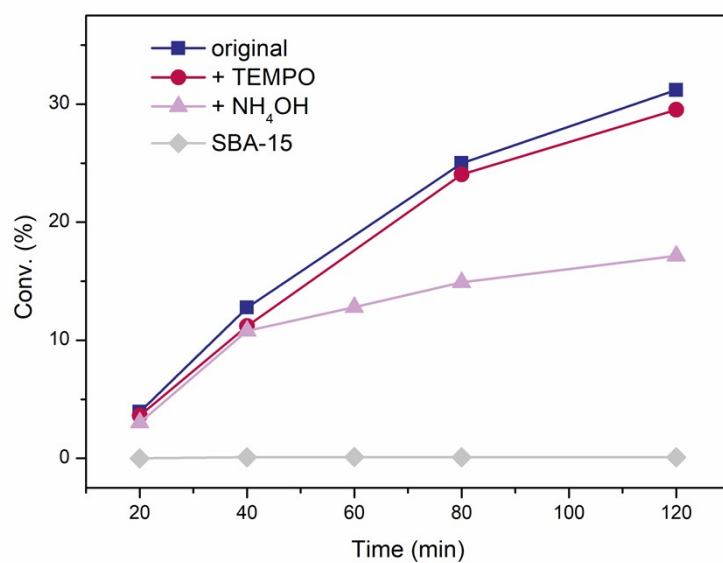


Fig. S8. Profiles of cis-cyclooctene epoxidation on WO₃-SBA-15 at different control conditions (Original reaction conditions: 50 mg of catalyst, 0.3 mL of cis-cyclooctene, 0.3 mL of H₂O₂ (30 wt%), 70 °C and 10 mL of acetonitrile).

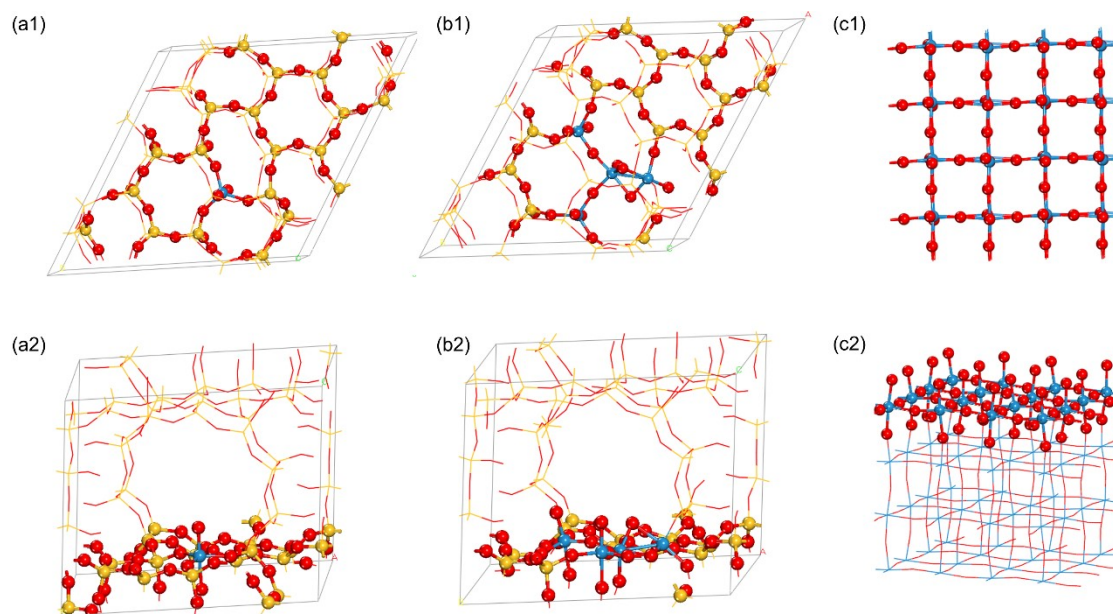


Fig. S9. The optimized structures of WO₃-SBA-15 (a1,a2), WO₃/SBA-15 (b1,b2) and Bulk-WO₃ (020) (c1,c2). The gold, blue and red represent Si, W and O atoms, respectively.

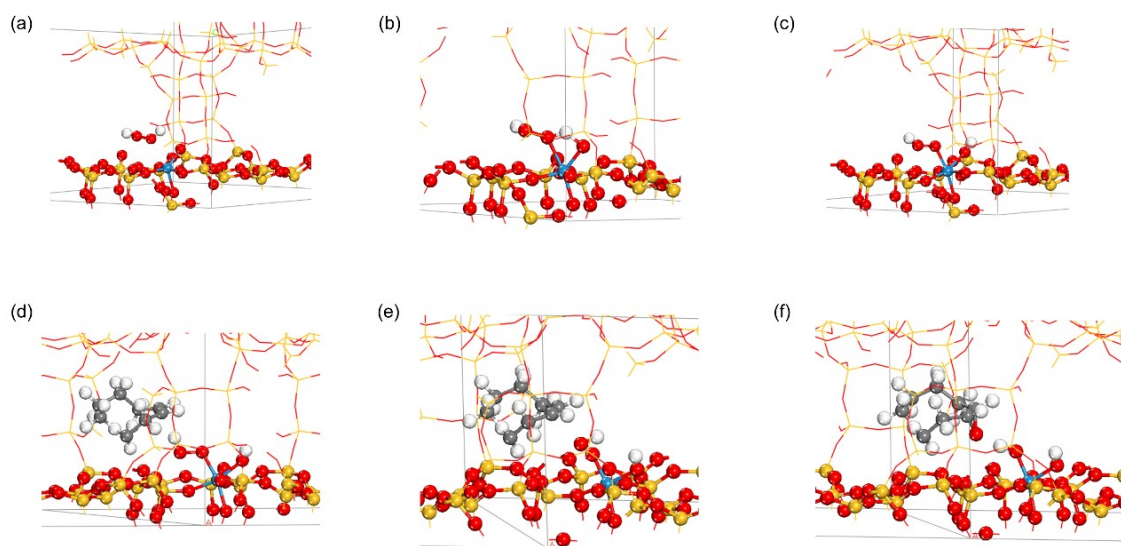


Fig. S10. Optimized structures of the adsorption of H₂O₂ (intermediate 2) (a), activation of H₂O₂ (TS1) (b), dissociation of H₂O₂ (intermediate 3) (c), the adsorption of cis-cyclooctene (intermediate 4) (d), O transfer (TS2) (e) and desorption of cis-cyclooctene oxide (intermediate 5) (f) on WO₃-SBA-15. The gold, red, blue, gray, and white spheres represent Si, O, W, C, and H atoms, respectively.

Reference

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