Supplementary information

Chemical deactivation of titanosilicates catalysts caused by propylene oxide in the HPPO process

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Supplementary information caption

Fig. S1 XRD patterns of Ti-MWW samples. (1): Ti-MWW, (2): Ti-MWW-PO, (3): Ti-MWW-PG, (4): Ti-MWW-MME, (5): Ti-MWW-$C_3^=$.

Fig. S2 SEM images of Ti-MWW samples.

Fig. S3 TEM images of Ti-MWW samples.

Fig. S4 UV-Vis spectra of Ti-MWW samples.

Fig. S5 Epoxidation of different olefins over Ti-MWW and Ti-MWW-PO.

Fig. S6 TGA curves of Ti-MWW-PO samples with different PO contents. Ti-MWW-PO-I-IV were treated by PO of different masses with 0.02 g, 0.04 g, 0.08 g, 0.10 g.

Fig. S7 Conversion (A)and concentration (B) of 1-hexene with under different Ti-MWW samples.

Fig. S8 The 1-hexene adsorption experiment of Ti-MWW-IV.

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Fig. S12 In-situ IR spectra of TS-1 catalyst recorded in He at 323 K (3 min, 10 min, and 25 min) after a period of 15 min of PO adsorption, (A): 4000−2500 cm^{-1}, (B): 1800−1500 cm^{-1}.

Fig. S13 UV-vis spectra of TS-1 (a), TS-1^s (b) and the corresponding deconvolution band at 203 nm and 235 nm. IR spectra in the hydroxyl stretching evacuated at 723 K of TS-1 samples in the range 3000−4000 cm^{-1} (c) ((1): TS-1, (2): TS-1^S).

Fig. S14 The lifetime in the epoxidation of propene over formed-Ti-MWW and formed-Ti-MWW-KCl.

Table S1 Catalytic performance of Ti-MWW$_{Bf}$-K samples for the epoxidation of 1-hexene.

Table S2 Lost weight of Ti-MWW-PO with different amounts of PO treatment.

Table S3 The initial reaction rate of Ti-MWW samples.

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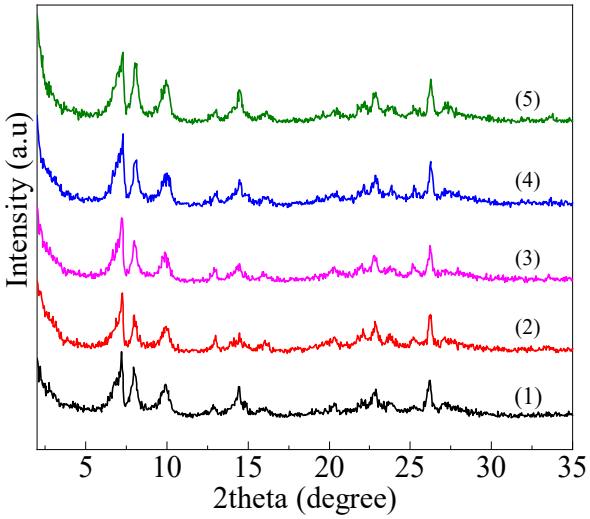

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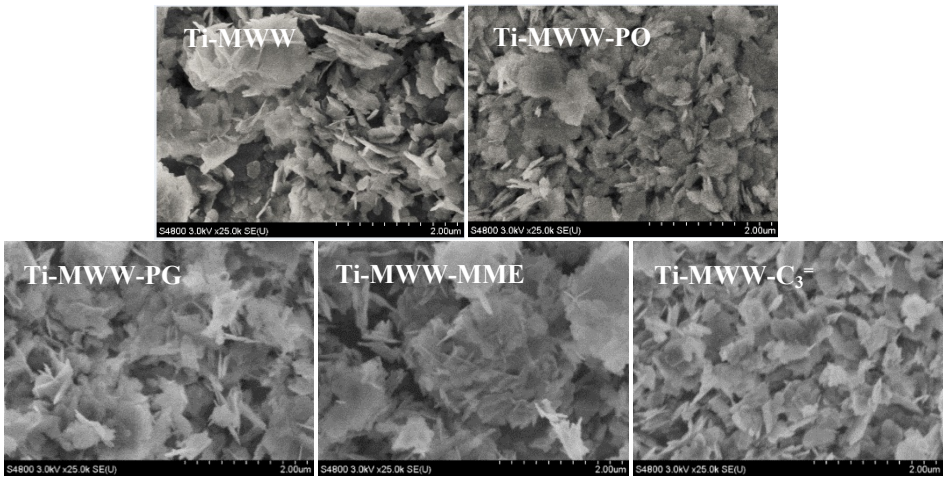


Fig. S2 SEM images of Ti-MWW samples.

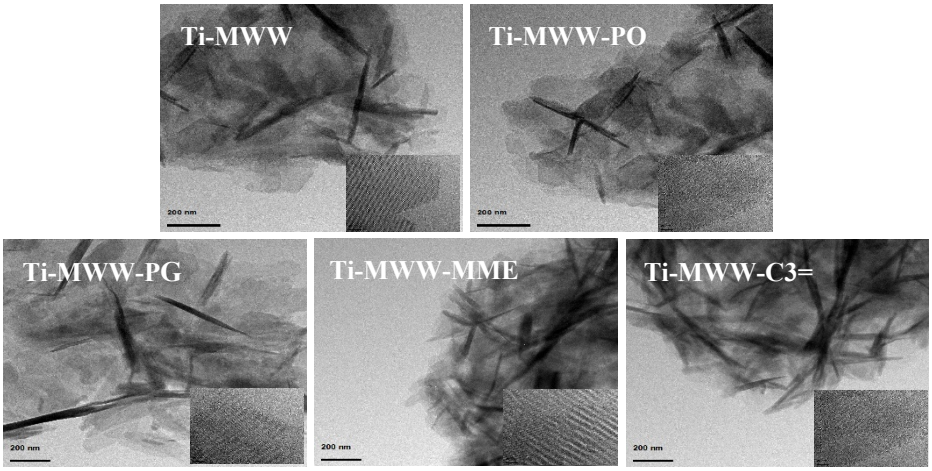


Fig. S3 TEM images of Ti-MWW samples.

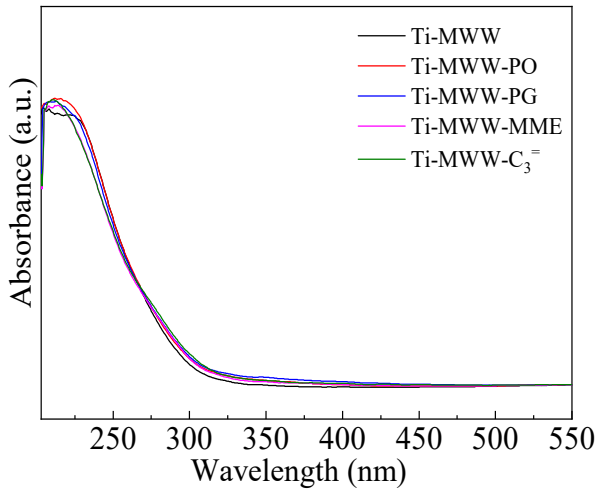


Fig. S4 UV-Vis spectra of Ti-MWW samples.

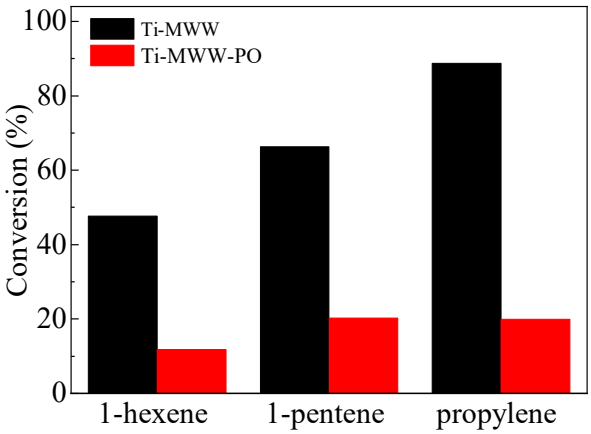


Fig. S5 Epoxidation of different olefins over Ti-MWW and Ti-MWW-PO.

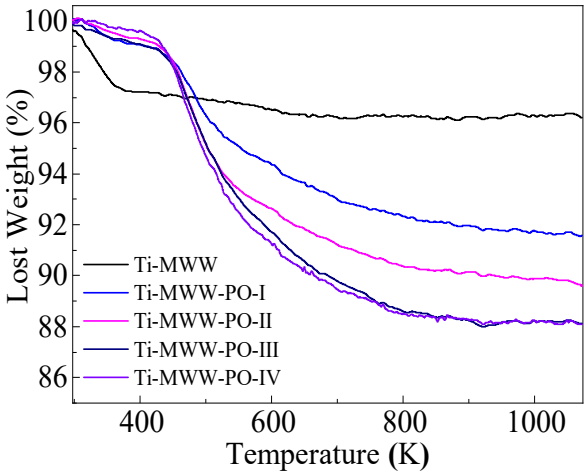


Fig. S6 TGA curves of Ti-MWW-PO samples with different PO contents. Ti-MWW-PO-I-IV were treated by PO of different masses with 0.02 g, 0.04 g, 0.08 g, 0.10 g.

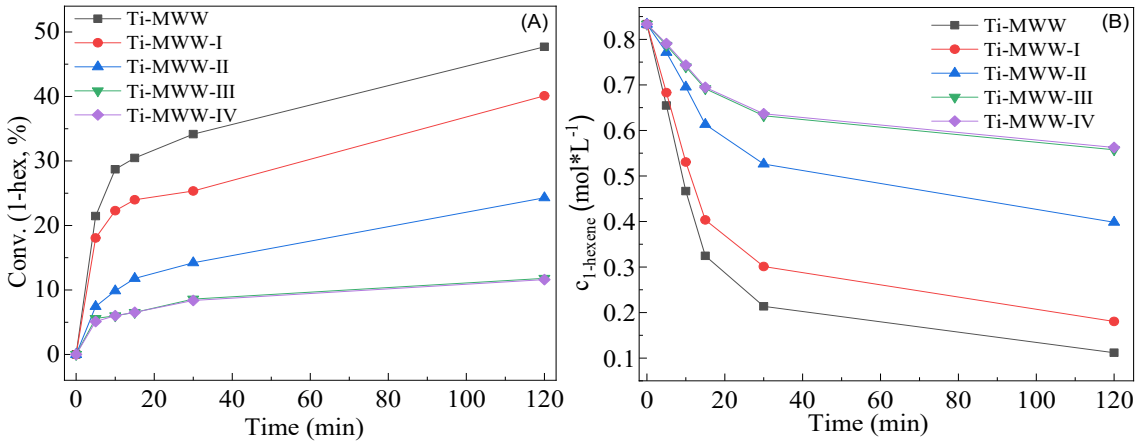


Fig. S7 Conversion (A)and concentration (B) of 1-hexene with under different Ti-MWW samples. Ti-MWW were post-treated by the different amount of PO (I: 0.02 g, II: 0.04 g, III: 0.08 g, IV:0.10 g.). Reaction conditions: catalyst 0.05 g, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3CN 10 mL, time 2 h, reaction temperature 60 °C.

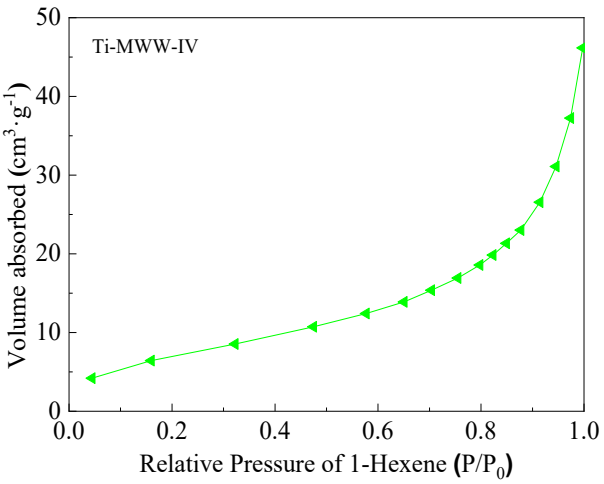


Fig. S8 The 1-hexene adsorption experiment of Ti-MWW-IV.

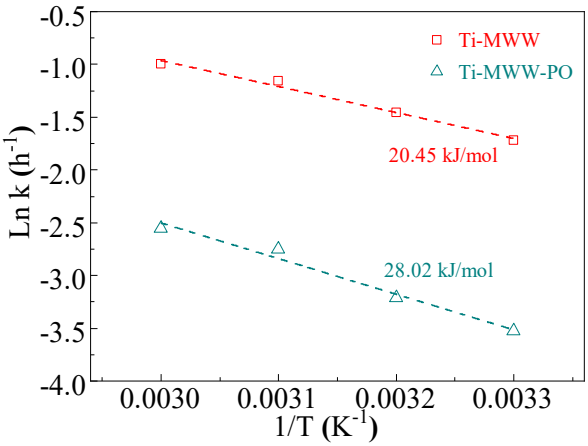


Fig. S9 Plots of apparent activation energy in the 1-hexene epoxidation catalyzed by Ti-MWW and Ti-MWW-PO.

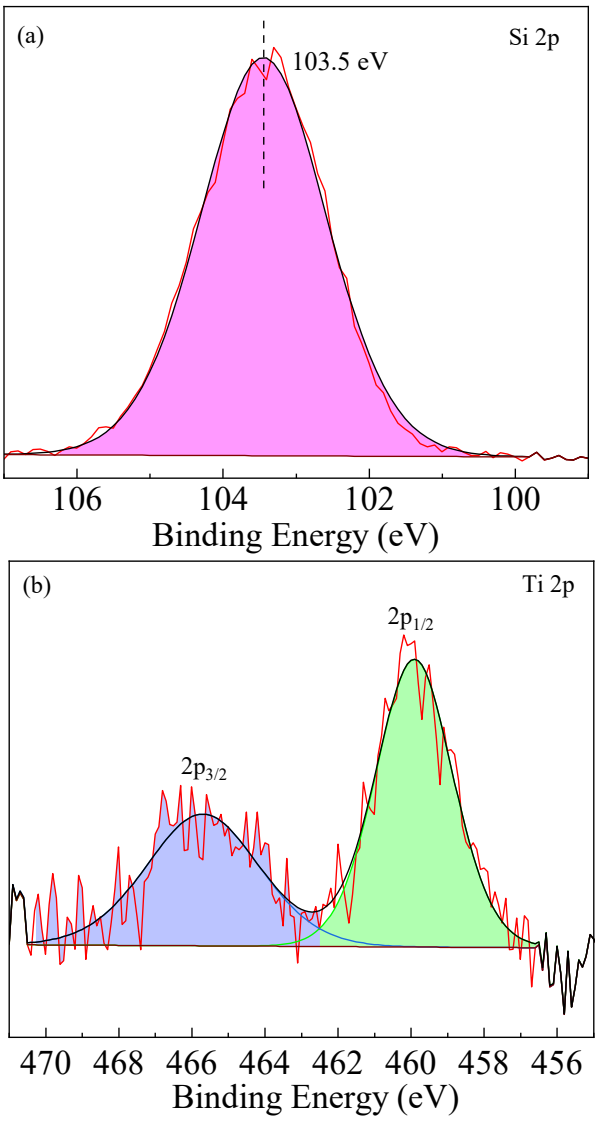


Fig. S10 XPS spectra of Ti-MWW.

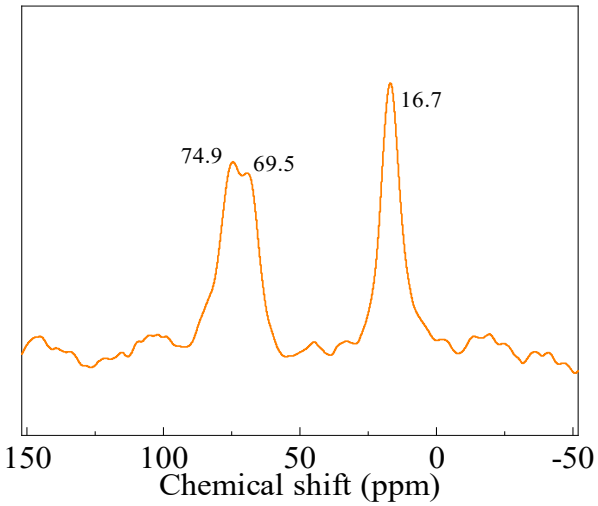
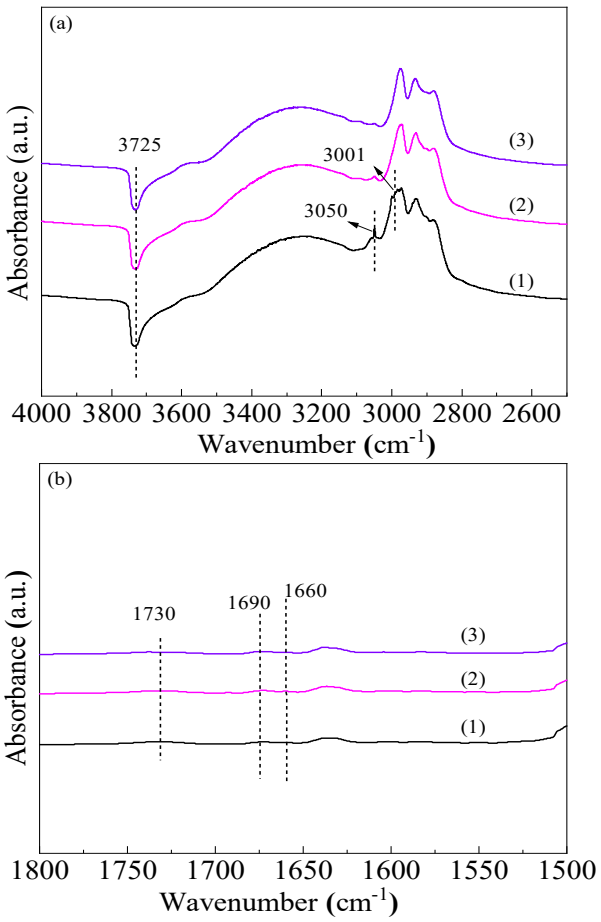


Fig. S11 ^{13}C solid-state MAS NMR spectrum of Ti-MWW-PO.



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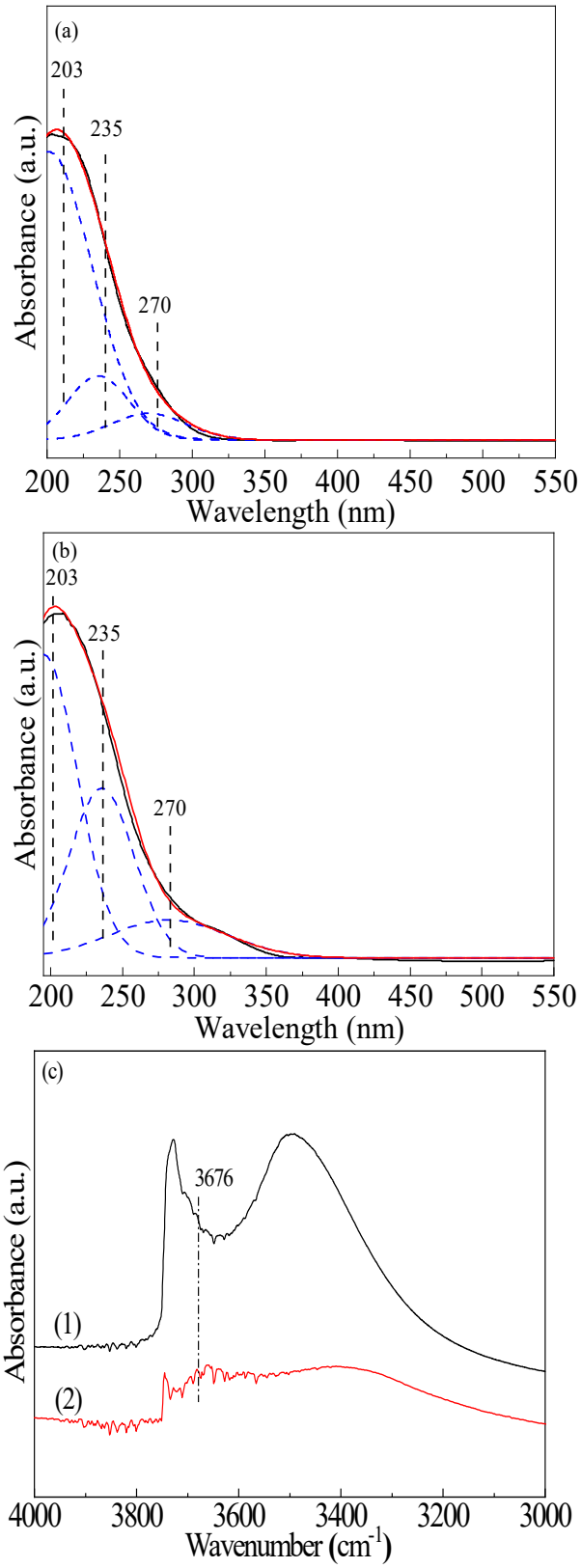

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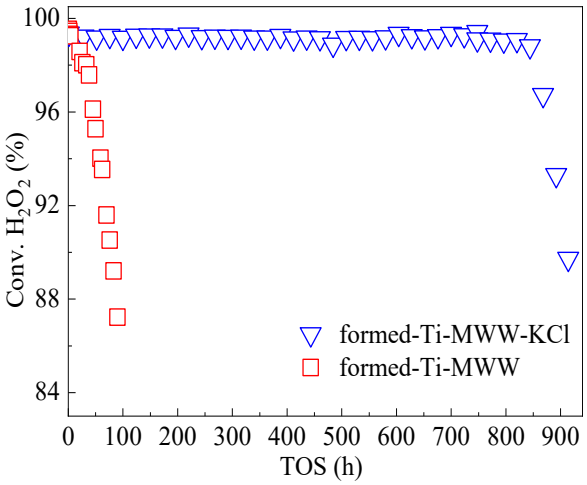

Fig. S14 The lifetime in the epoxidation of propene over formed-Ti-MWW and formed-Ti-MWW-KCl.

Table S1 Catalytic performance of Ti-MWW_{Bf}-K samples for the epoxidation of 1-hexene.

Samples	[a] TON	[b] Conv.(1-hex.)/%	[b] Conv.(H_2O_2)/%	[b] Sel.(Epo.)/%	[b] Eff.(H_2O_2)/%	[c] K/Ti
Ti-MWW_{Bf}-K(A)	281	75.5	85.5	100	88.3	0.39
Ti-MWW_{Bf} -K(B)	46	12.3	20.4	100	60.4	1.91

[a] Turnover number (TON) of converted 1-hexene per Ti site in mol per mol Ti. [b] Reaction conditions: catalyst 0.05 g, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3CN 10 mL, time 2 h, reaction temperature 60 °C. [c] Detected by ICP.

Table S2 Lost weight of Ti-MWW-PO with different amounts of PO treatment.

[a] Sample	[b] 298~373 K/%	[b] 373~923 K/%	[b] Total weight loss/%
Ti-MWW	2.42	1.07	3.49
Ti-MWW-PO-I	0.77	7.11	7.88
Ti-MWW-PO-II	0.54	9.49	10.0
Ti-MWW-PO-III	0.45	11.35	11.8
Ti-MWW-PO-IV	0.43	11.47	11.9

[a] Ti-MWW-PO-I-IV were treated by PO of different masses with 0.02 g (I), 0.04 g (II), 0.08 g (III), and 0.10 g (IV). [b] Calculated by TG curves (Fig. S5).

Table S3 The initial reaction rate of Ti-MWW samples.

Sample	[a] $r_{0(}$epo) mol/(L*g*min)
Ti-MWW	0.686
Ti-MWW-I	0.576
Ti-MWW-II	0.294
Ti-MWW-III	0.190
Ti-MWW-IV	0.186

[a] In addition, the initial reaction rates (r_0(epo)) were calculated from tangential slopes at reaction time (t) = 0 using exponential curve fitting.

Table S4 Catalytic performance for the epoxidation of 1-hexene with H_2O_2.

Samples	[a] Conv.(1-hex.)/%	[a] Conv.(H_2O_2)/%	[a] Sel.(Epo)/%	[a] Eff.(H_2O_2)/%	[b] TON
TS-1-80	13.1	16.1	95.3	75.6	127
TS-1-80-PO	10.6	17.1	97.2	62.0	103
[c] TS-1^s	23.0	29.6	95.0	74.5	224
[c] TS-1^s-PO	16.6	29.5	98.2	55.1	162

[a] Reaction conditions: catalyst 0.05 g, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3CN 10 mL, time 2 h, reaction temperature 60 °C. [b] Turnover number (TON) of converted 1-hexene per Ti site in mol per mol Ti. [c] TS-1^s was treated with ethylamine (EA) at 443 K.