

†Electronic Supplementary Information (ESI)

**Highly selective 1-pentene epoxidation over Ti-MWW with modified
micro-environment of Ti active sites**

Jinpeng Yin, Hao Xu*, Bowen Wang, Wenwen Tian, Jianyong Yin, Jingang Jiang, Peng Wu*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and

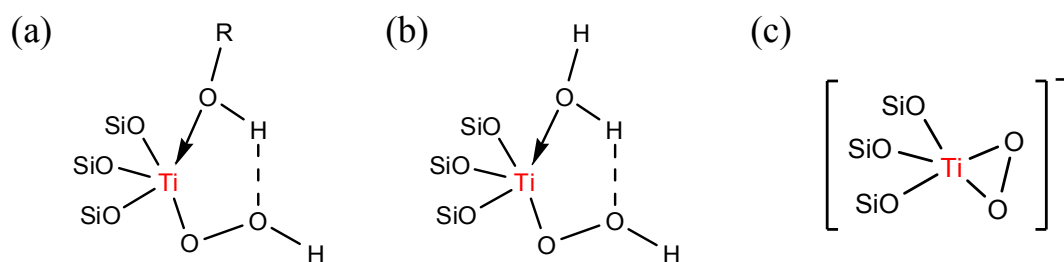
Molecular Engineering, East China Normal University, Shanghai 200062, China

Tel: +86-21-6223-2292

Fax: +86-21-6223-2292

E-mail: hxu@chem.ecnu.edu.cn (H. Xu); pwu@chem.ecnu.edu.cn (P. Wu).

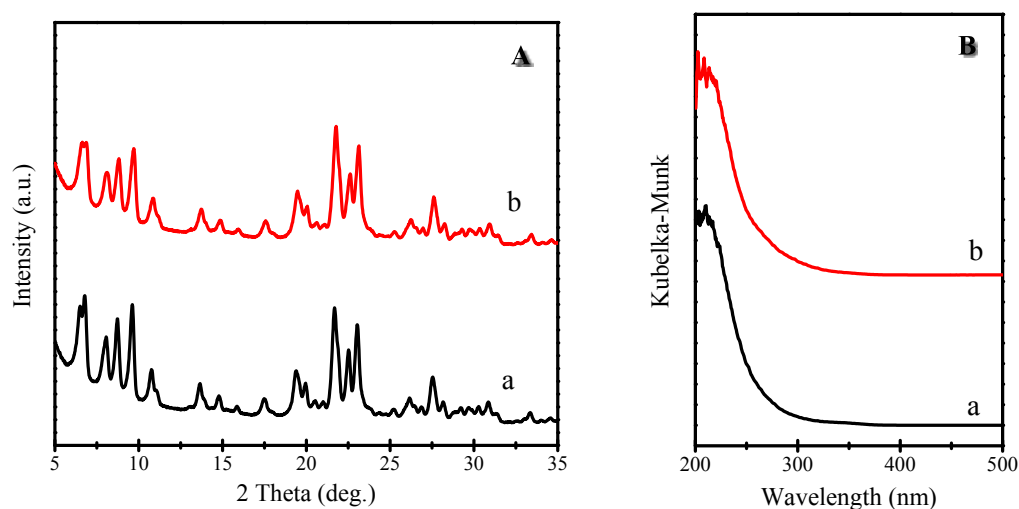
Fax: +86-21 62232292



Scheme S1. Five-membered ring hydroperoxo Ti-O-O-H intermediate species formed in protic alcohol solvent (a), and in aprotic solvent (b), and peroxo Ti-(η^2 -O₂) intermediate (c). In aprotic solvent like acetonitrile, the water molecules from aqueous hydrogen peroxide participate in the construction of Ti-O-O-H active species.

Table S1. The textural properties of various titanasilicates.

Catalyst	Structure code	Channels or pores	Si/Ti ^a	Crystal size ^b (μm)	SSA ^c ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	
						$V_{\text{total}}^{\text{d}}$	$V_{\text{mic}}^{\text{e}}$
Ti-MCM-68	MSE	12 $\times$ 10 $\times$ 10, 12 $\times$ 18 cage	74	0.05-0.1	572	0.36	0.19
Ti-MWW	MWW	10-10, 12 $\times$ 18 cage	40	0.6 $\times$ 0.6 $\times$ 0.1	552	0.46	0.15
TS-1	MFI	10 $\times$ 10	35	0.4-0.5	545	0.42	0.13
TS-2	MEL	10 $\times$ 10	54	0.05 $\times$ 0.4	539	0.40	0.12
Ti-Beta	*BEA	12 $\times$ 12 $\times$ 12	50	0.05-0.15	615	0.54	0.17
Ti-MOR	MOR	12-8	56	0.2-0.5	514	0.35	0.16

^a Determined by ICP analysis.^b Evaluated by SEM images.^c Specific surface are (SSA), determined by nitrogen adsorption isotherms at 77 K using Langmuir method.^d Total pore volume (V_{total}), calculated from the N_2 adsorption volume at $P/P_0 = 0.99$.^e Micropore volume (V_{mic}), calculated with t -plot method.**Fig. S1.** XRD patterns (A) and UV-Vis spectra (B) of fresh Ti-MCM-68 (a) and spent Ti-MCM-68 (b).

The Si/Ti molar ratio of Ti-MCM-68 was 74 before and after reaction (determined by ICP analysis).

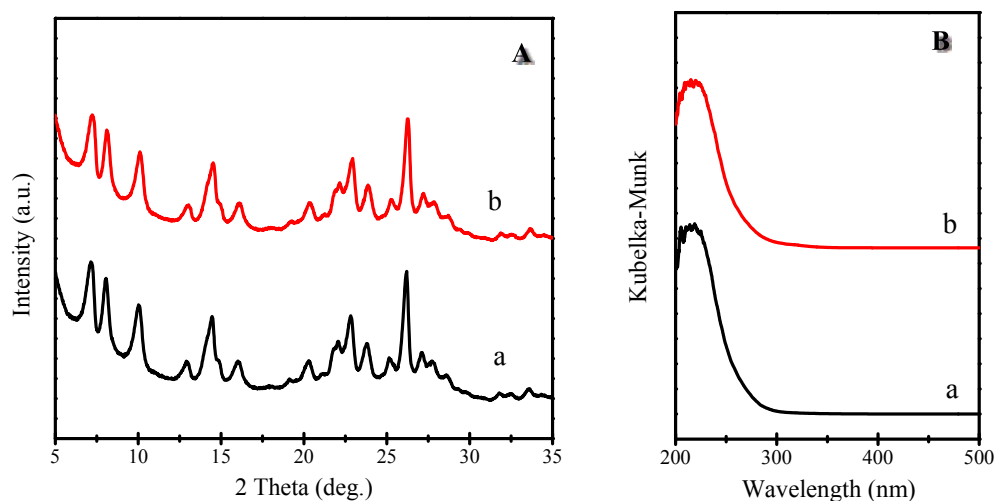


Fig. S2. XRD patterns (A) and UV-Vis spectra (B) of fresh Ti-MWW (a) and spent Ti-MWW (b).

The Si/Ti molar ratio of Ti-MWW was 40 before and after reaction (determined by ICP analysis).

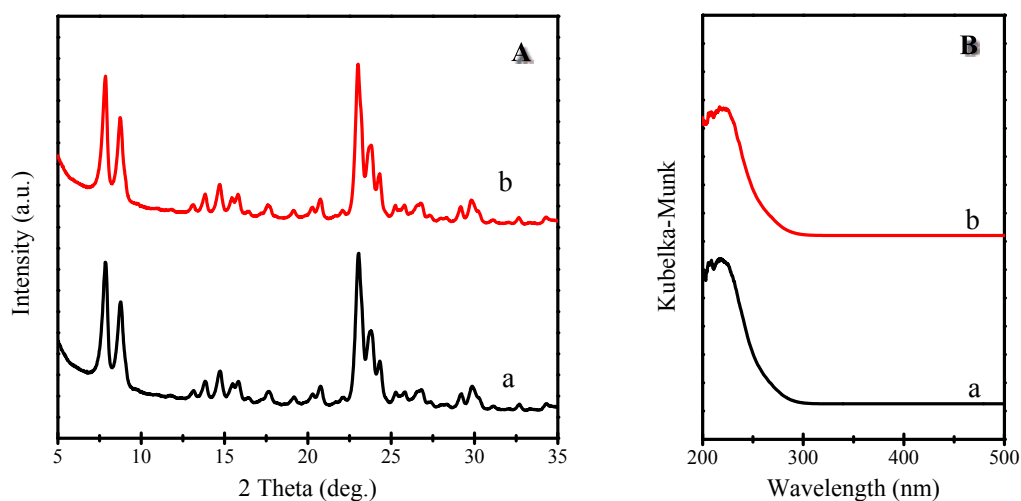


Fig. S3. XRD patterns (A) and UV-Vis spectra (B) of fresh TS-1 (a) and spent TS-1 (b).

The Si/Ti molar ratio of TS-1 was 35 before and after reaction (determined by ICP

analysis).

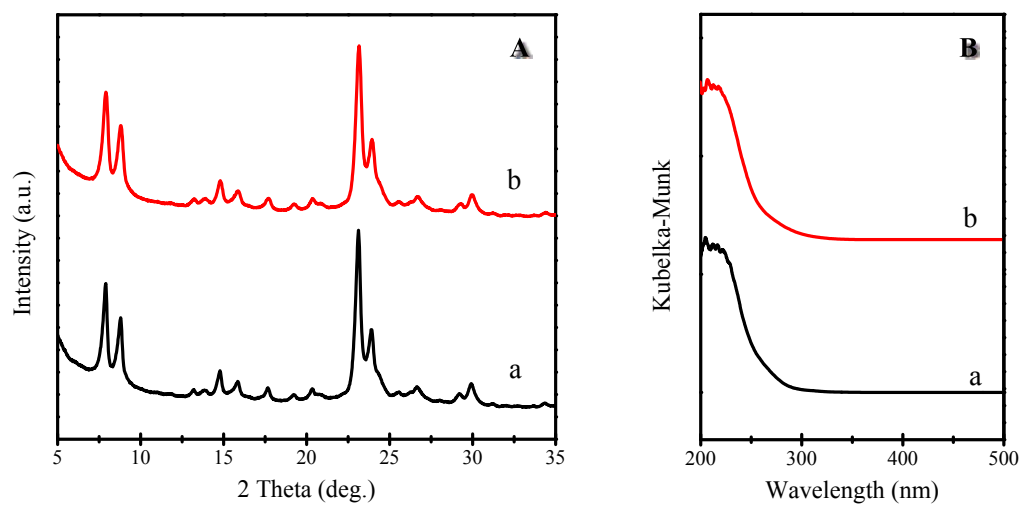


Fig. S4. XRD patterns (A) and UV-Vis spectra (B) of fresh TS-2 (a) and spent TS-2 (b).

The Si/Ti molar ratio of TS-2 was 54 before and after reaction (determined by ICP analysis).

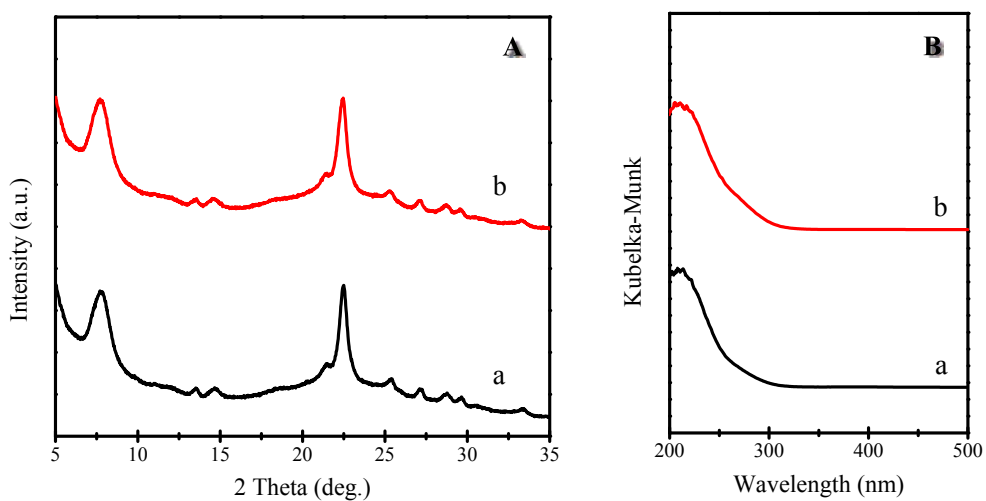


Fig. S5. XRD patterns (A) and UV-Vis spectra (B) of fresh Ti-Beta (a) and spent Ti-Beta (b).

The Si/Ti molar ratio of Ti-Beta was 50 before and after reaction (determined by ICP analysis).

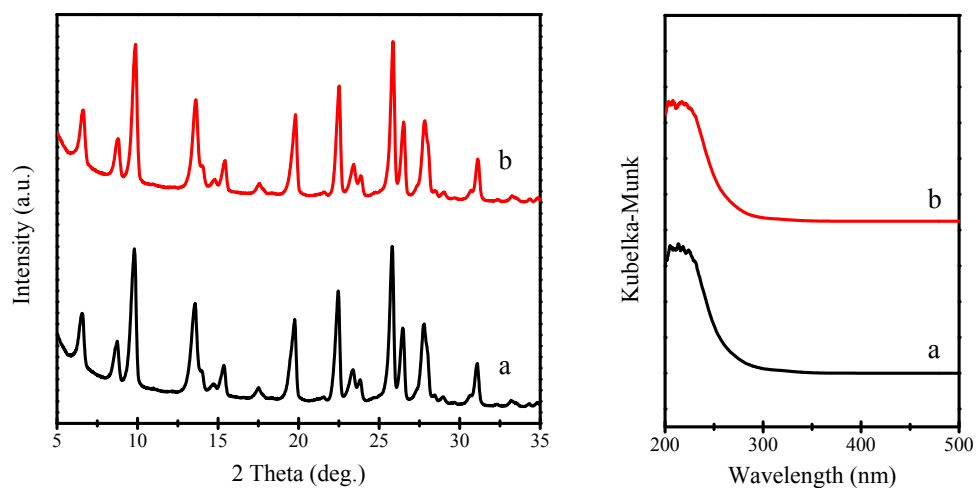


Fig. S6. XRD patterns (A) and UV-Vis spectra (B) of fresh Ti-MOR (a) and spent Ti-MOR (b).

The Si/Ti molar ratio of Ti-MOR was 56 before and after reaction (determined by ICP analysis).

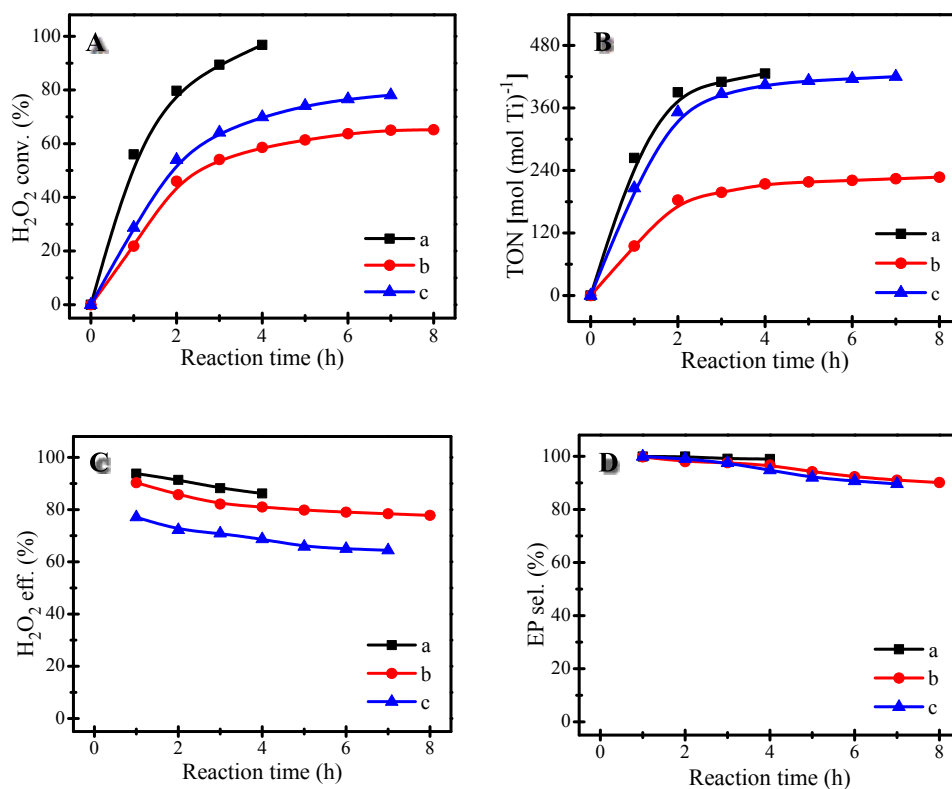
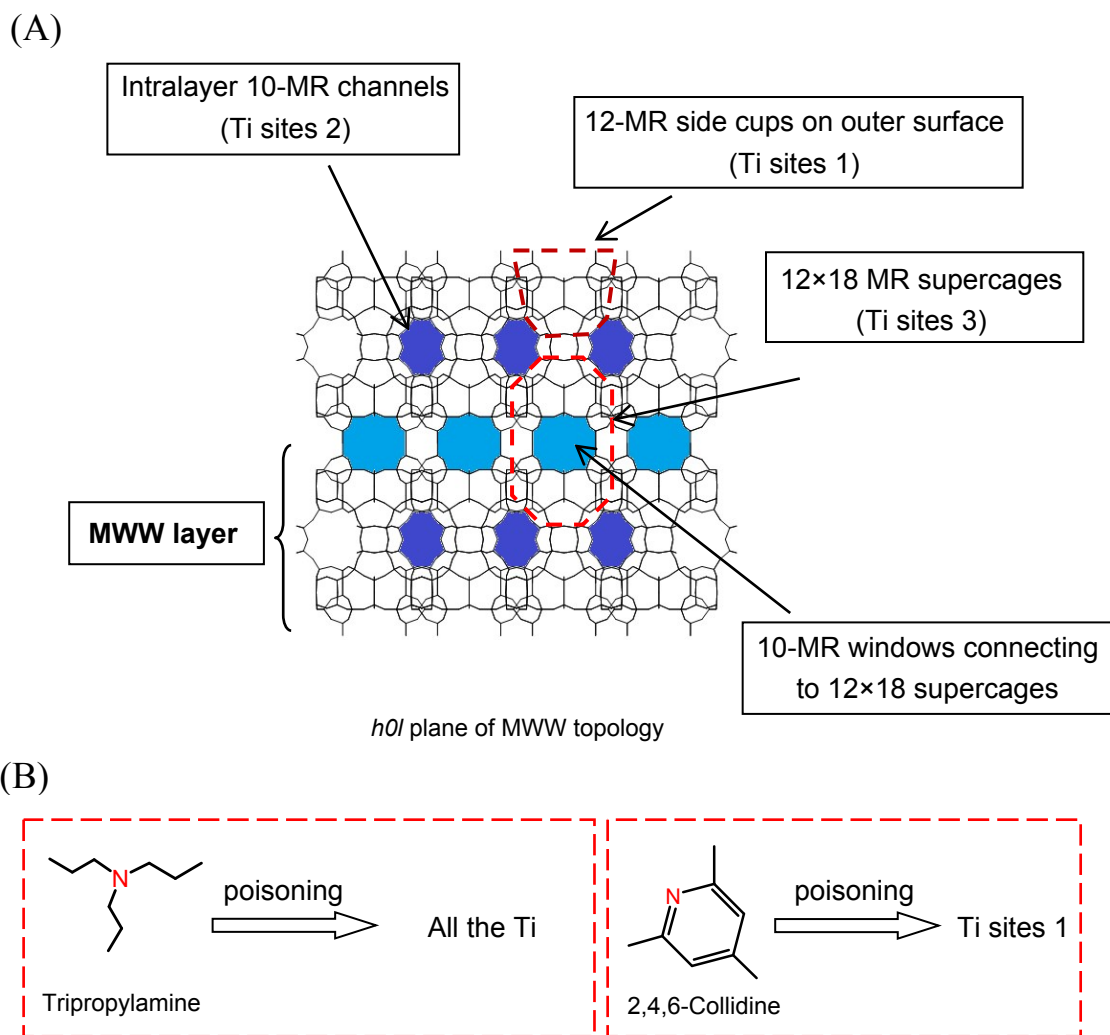


Fig. S7. Dependence of H_2O_2 conversion (A), TON value (B), H_2O_2 utilization efficiency (C), and EP selectivity (D) on reaction time over Ti-MWW (a), TS-1 (b) and Ti-MCM-68 (c). Reaction conditions: cat., 50 mg; solvent, 10 mL; MeCN for Ti-MWW and Ti-MCM-68, while MeOH for TS-1; H_2O_2 (30 wt.%), 10 mmol; 1-pentene, 10 mmol; N_2 , 0.5 MPa; temp., 333 K.



Scheme S2. Ti sites in Ti-MWW framework (A), and selective Ti-poisoning experiments (B).

Table S2. The catalytic performance of selective poisoned Ti-MWW in 1-pentene epoxidation.^a

Catalyst	Poisoning reagent	1-Pentene conv. (%)	Epoxide sel. (%)	H ₂ O ₂ (%)	
				conv.	eff.
Ti-MWW	None	72.9	99.9	79.7	91.5
	TPA	1.4	86.3	30.8	4.5
	COD	70.6	99.9	78.5	89.9

^a Reaction conditions seen in Tab.3. Poisoning reagent, 2 mmol; TPA, tripropylamine; COD, 2,4,6-collidine.

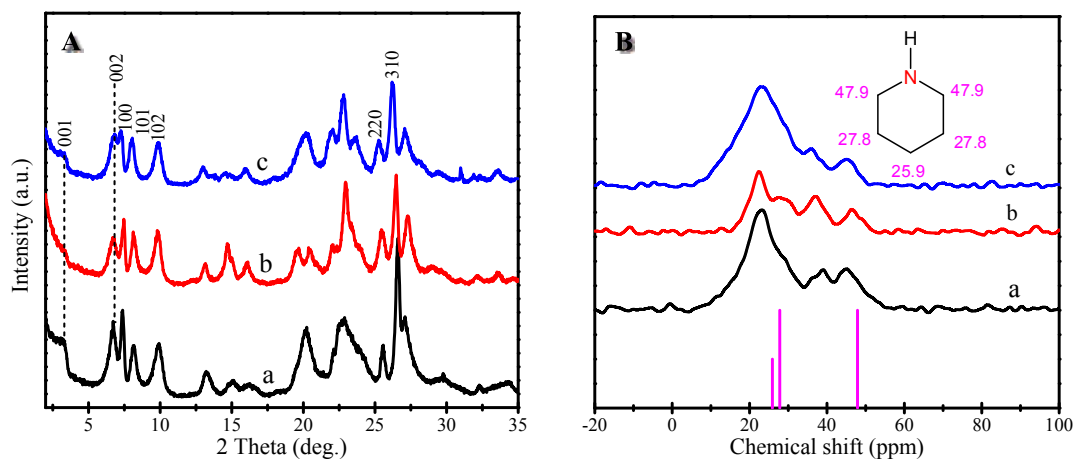


Fig. S8. XRD patterns (A) and ¹³C MAS NMR spectra (B) of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).

Table S3. Reaction results of 1-pentene epoxidation over Ti-MWW with piperidine addition.^a

Catalyst	Piperidine	1-Pentene conv. (%)	EP sel. (%)	H ₂ O ₂ (%)	
				conv.	eff.
Ti-MWW	Yes	24.2	98.5	27.2	89.0
	No	72.9	99.9	79.7	91.5

^a: Reaction conditions: catalyst, 50 mg; 1-pentene, 10 mmol; H₂O₂ (30 wt.%), 10 mmol; piperidine, 0.07 mmol, which was equal to the amount that occluded in R-Ti-MWW given by TG analysis; temp. 333 K; N₂, 0.5 MPa; MeCN, 10 mL; time 2 h.

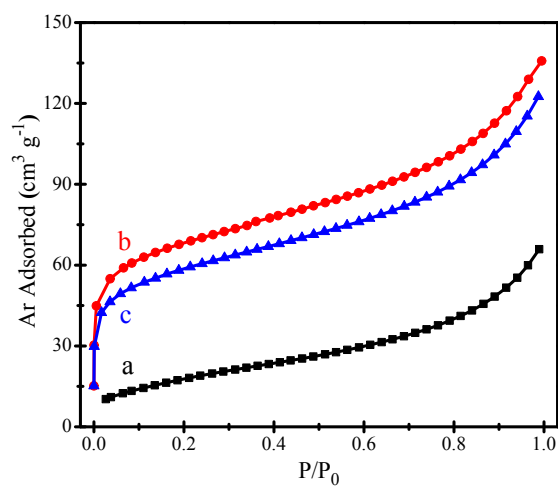


Fig. S9. Ar adsorption isotherms of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).

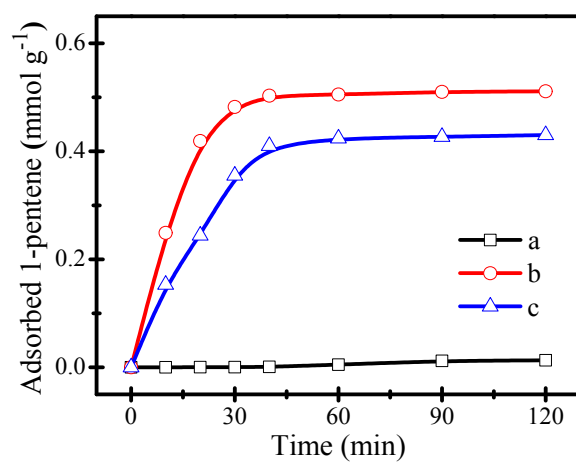


Fig. S10. Liquid-phase 1-pentene adsorption with time of stream on the PI-containing P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c) zeolite. Adsorption conditions: catalyst, 0.1 g; 1 wt.% 1-pentene in 1,3,5-TIPB, 3 g; temp., 298 K.

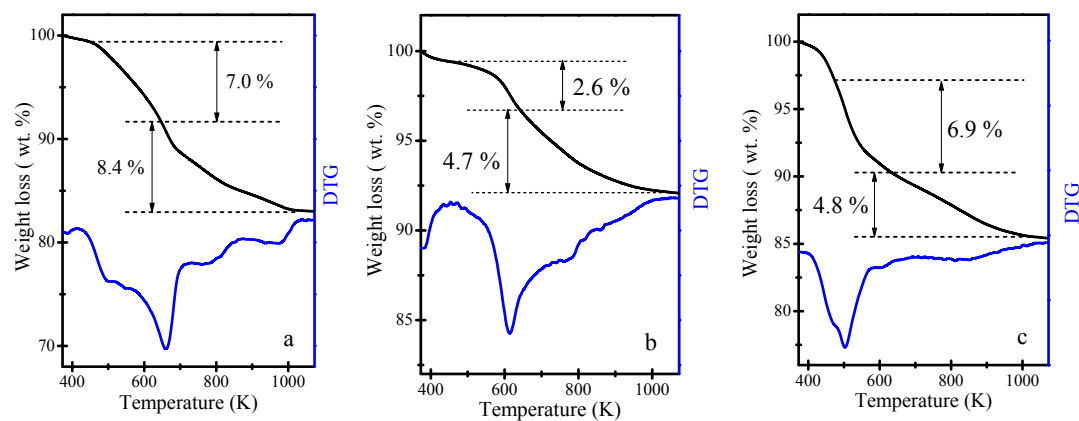
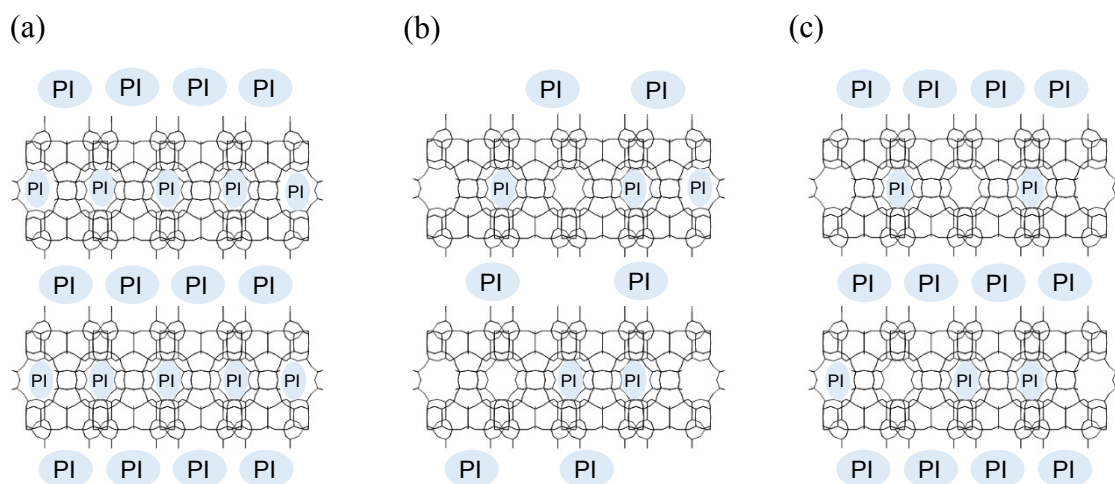
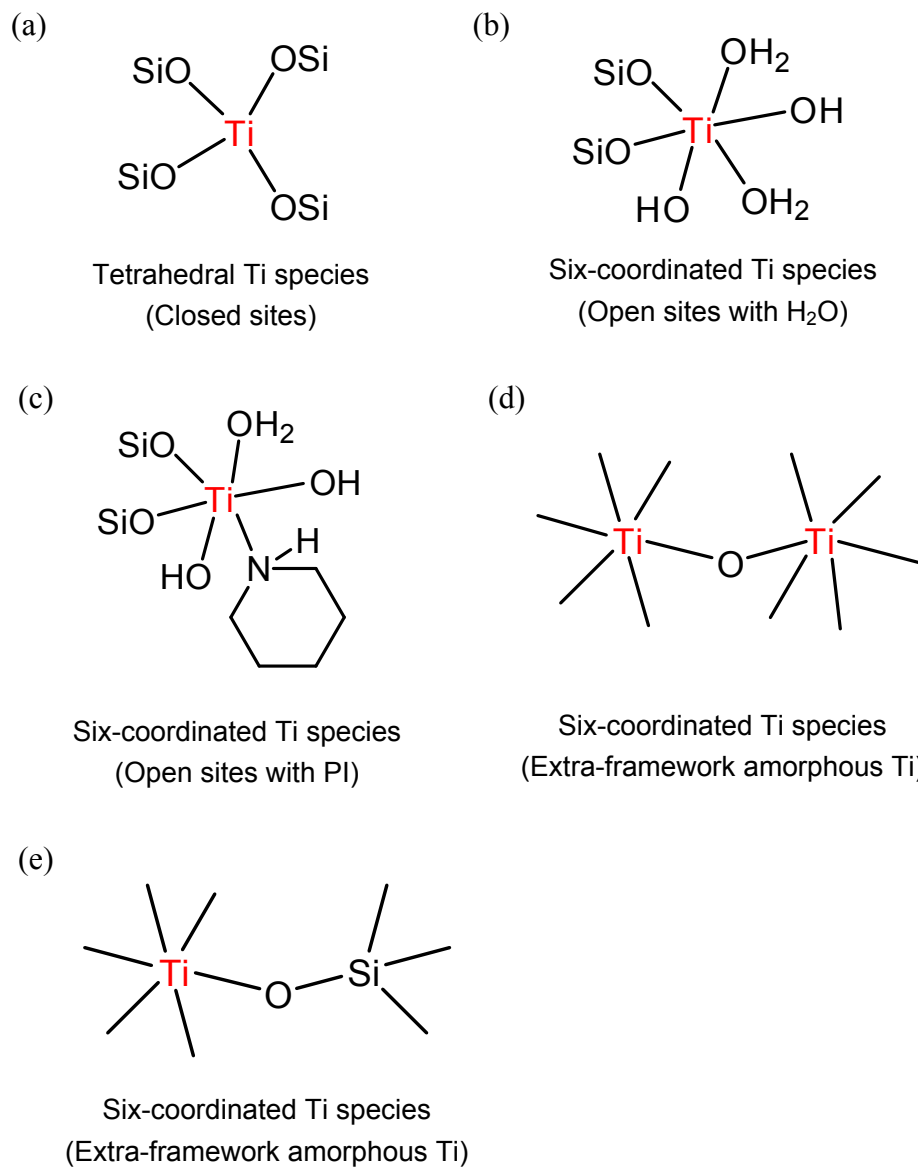


Fig. S11. TG-DTG curves of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).



Scheme S3. Possible structures of 2D Ti-MWW containing PI molecules: P-Ti-MWW(a); A-Ti-MWW (b) and R-Ti-MWW (c).



Scheme S4. The proposed coordination of Ti species: tetrahedral Ti species (a); hexa-coordinated Ti species with H₂O (b); hexa-coordinated Ti species with PI (c) and extra-framework amorphous Ti species (d, e).

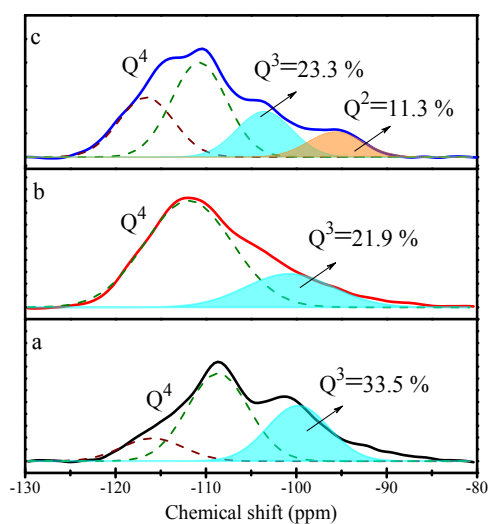


Fig. S12. ^{29}Si MAS NMR spectra of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).

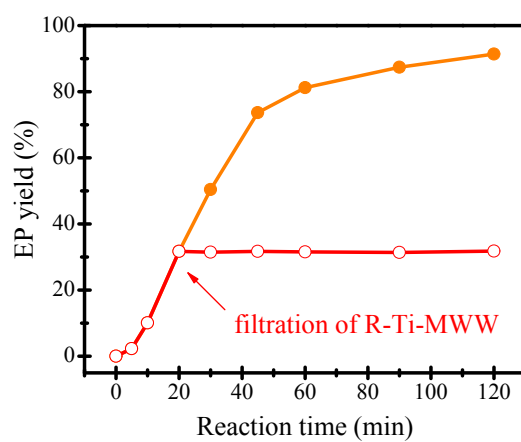


Fig. S13. Hot filtration test for 1-pentene epoxidation with H_2O_2 over R-Ti-MWW.

Reaction conditions seen in Fig. 9.

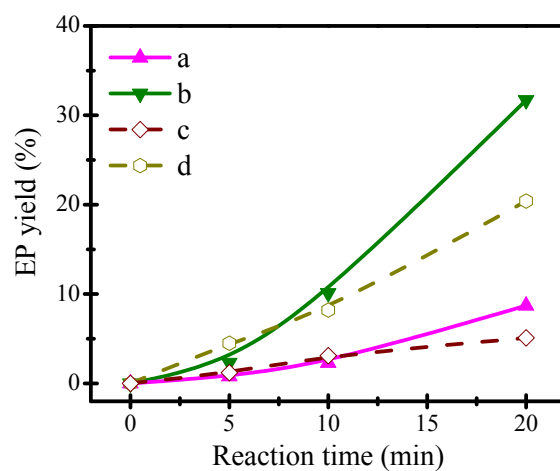


Fig. S14. A comparison of catalytic performance in 1-pentene epoxidation with time course over the different Ti-MWW zeolites. Reaction conditions: catalyst, 50 mg; 1-pentene, 15 mmol; oxidant, 15 mmol, wherein H_2O_2 (30 wt %) was used for Ti-MWW (a) and R-Ti-MWW (b), and TBHP (70 wt.% in water) was also employed for Ti-MWW (c) and R-Ti-MWW (d); solvent MeCN, 10 mL; temp. 333 K, N_2 , 0.5 MPa. The EP selectivity was always >99 % for all the reactions.

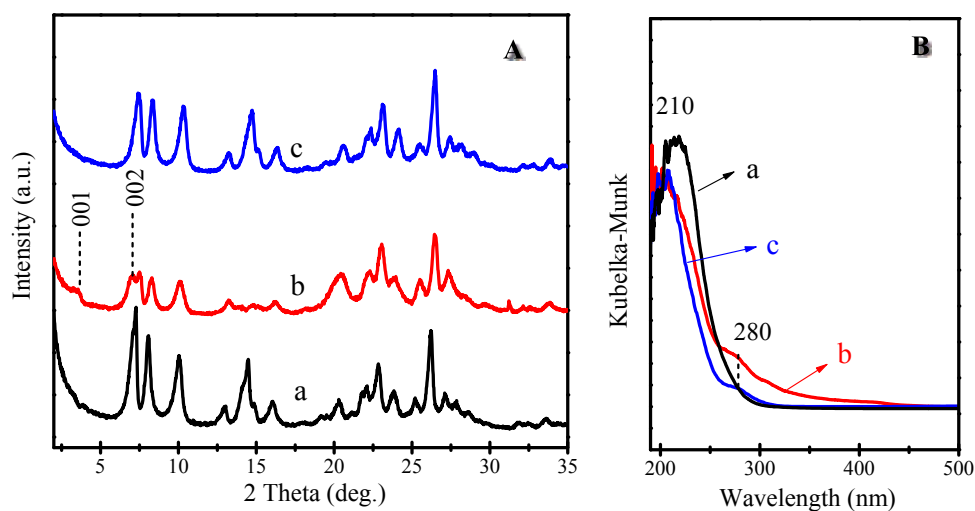


Fig. S15. XRD patterns (A) and UV-Vis spectra (B) of Ti-MWW (a), R-Ti-MWW (b) and R-Ti-MWW-cal (c).

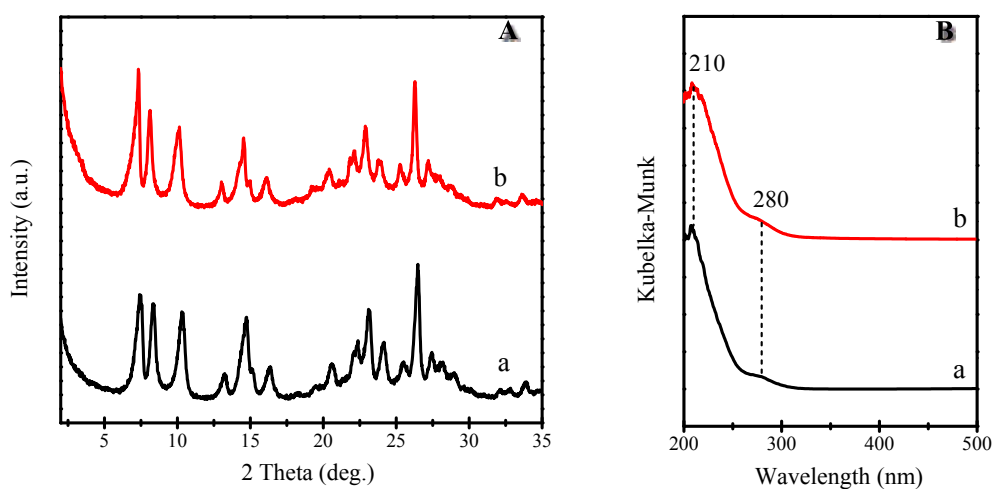


Fig. S16. XRD patterns (A) and UV-Vis spectra (B) of fresh R-Ti-MWW-cal (a) and spent R-Ti-MWW-cal (b).

The Si/Ti molar ratio of R-Ti-MWW-cal was 41 before and after reaction (determined by ICP analysis).

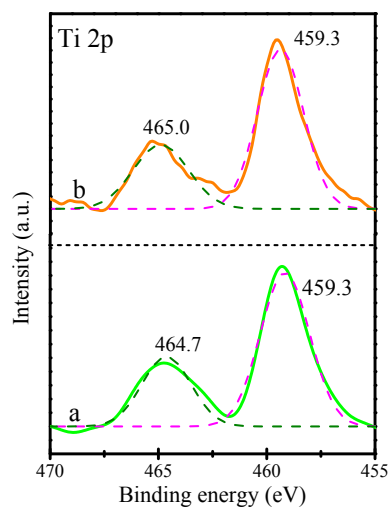


Fig. S17. Ti 2p XPS spectra of R-Ti-MWW (a) and R-Ti-MWW-cal (b).

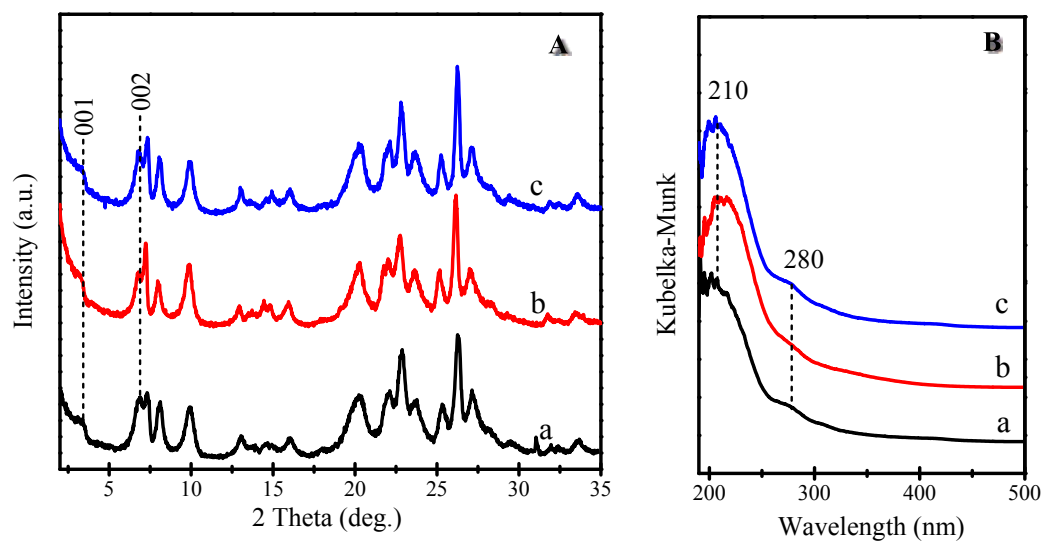


Fig. S18. XRD patterns (A) and UV-Vis spectra (B) of fresh R-Ti-MWW (a), deactivated R-Ti-MWW after 6 runs (b) and Regenerated R-Ti-MWW (c).

The R-Ti-MWW catalyst was considered deactivated after six runs, and the catalyst was subjected to regeneration after being used for eight times.

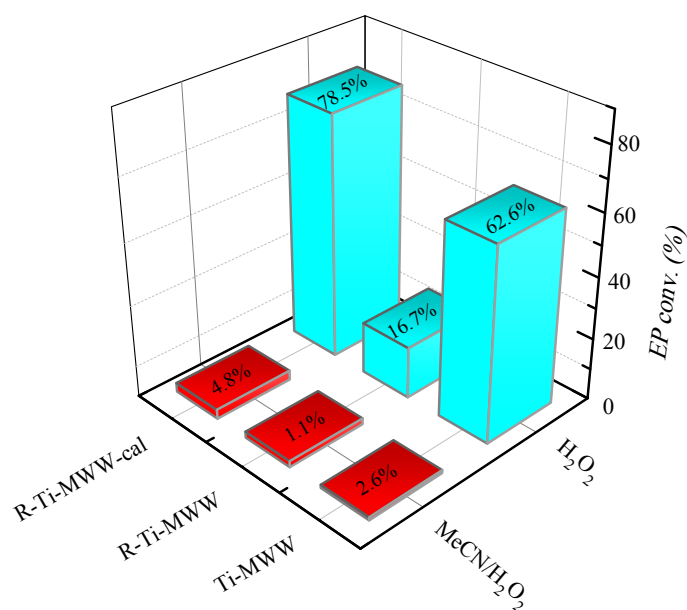


Fig. S19. A comparison of EP conversion among Ti-MWW, R-Ti-MWW and R-Ti-MWW-cal in the ring-opening reaction of EP in MeCN/H₂O₂ or H₂O₂ system. Reaction conditions: catalyst, 0.1 g; EP, 10 mmol; H₂O₂ (30 wt.%), 10 mmol; H₂O/EP molar ratio, 20; temp., 333 K; N₂, 0.5 MPa; MeCN (if added), 10 mL; time 4 h.

In comparison to the H₂O₂ system, the EP conversion of all the catalysts was pretty low in the MeCN/H₂O₂ system, indicating solvent MeCN could inhibit the hydrolysis of EP very well.

Compared with Ti-MWW, the EP conversion of R-Ti-MWW-cal was higher in both MeCN/H₂O₂ and H₂O₂ system, possibly due to the higher Lewis acid content in R-Ti-MWW-cal as revealed by the pyridine-adsorbed IR spectra in Fig. S20.

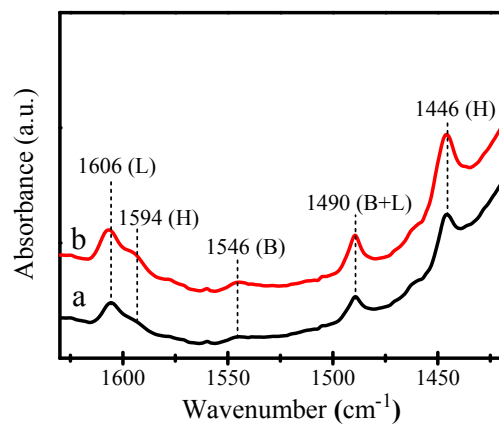


Fig. S20. Pyridine-adsorbed IR spectra after evacuation at 473 K for 0.5 h of Ti-MWW(a) and R-Ti-MWW-cal (b).