Electronic Supplementary Information (ESI) For

Synthesis of highly active oxidation catalyst with improved distribution of titanium coordination states

Lizhi Wu,[a] Xiujuan Deng,[a] Shufang Zhao,[a] Hanmei Yin,[a] Zuoxi Zhuo,[a] XiangQing Fang,[b] Yueming Liu,*[a] and Mingyuan He[a]

[a] L. Wu, Dr. X. Deng, S. Zhao, H. Yin, Dr. Z. Zhuo, Prof. Y. Liu, Prof. M. He

Shanghai Key Laboratory of Green Chemistry and Chemical Processes

School of Chemistry and Molecular Engineering

East China Normal University

North Zhongshan Rd. 3663, Shanghai 200062, P. R. China

E-mail: *ymliu@chem.ecnu.edu.cn*

[b] Dr. X. Fang

Xi`an Aeronautical University

No.259, West 2nd Ring, Lianhu District, Xi'an City, Shaanxi Province 710077, P. R. China

Experimental section

1. The preparation of titanosilicate catalysts

1.1 synthesis of TS-1 and TS-2

TS-1 was hydrothermally synthesized following the literature (X. Deng, Y. Wang, L. Shen, H. Wu, Y. Liu, M. He, *Ind. Eng. Chem. Res.* 2013, **52**, 1190). A typical synthesis of TS-1 in a two-step hydrolysis method is as follows. In the first step, a mixture of partial TEOS and all TBOT was added dropwise into TPAOH solution under stirring at room temperature. After hydrolyzing at 323 K for 30 min and removing alcohols by evaporation at 353 K, the obtained clear sol has the following molar composition: 1.0 SiO_2:(0.013−0.033) TiO_2:(0.18~0.25) TPAOH:18 H_2O. In the second step, when the sol was cooled down, the Si-Sol was added dropwise. The composition of the final sol was maintained in the range of 1.0 SiO_2:(0.0064−0.016) TiO_2:(0.1~0.15) TPAOH:18 H_2O. Then it was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 443 K for 2 days. Afterward, the product was recovered by filtration, washed with distilled water, dried at 363 K overnight, and finally calcined at 823 K for 6 h. The calcined sample was denoted TS-1-(Si/Ti). If not special specified, the Si/Ti in TS-1 was 82.

TS-2 (Si/Ti = 54) was prepared according to the literature (J.S. Reddy, R. Kumar, P. Ratnasamy, *Appl. Catal.* 1990, **58**, L1).

1.2 Synthesis of TS-1$^+$ and TS-2$^+$

TS-1-(Si/Ti)$^+$ or TS-2-(Si/Ti)$^+$ was synthesized through post-treatment of the conventional sample TS-1-(Si/Ti) or TS-2-(Si/Ti). TS-1-(Si/Ti) or TS-2-(Si/Ti) was suspended in an aqueous solution that contained TPABr and ethylamine (EA) in a PTFE lining, the typical aqueous solution has the following molar composition: 1.0 SiO_2: 0.04 TPABr: 0.07 EA:10 H_2O. Then the mixture was stirred for half an hour. The PTFE lining was put into a stainless-steel autoclave and crystallized at 443 K for 24h. And the corresponding synthesis conditions [TPABr/SiO_2 (0-0.07)，EA/SiO_2 (0-0.14), crystallization time (2-48 h), crystallization temperature (393-463 K)] were investigated in detail. Then the product was recovered by filtration, drying, and calcinations (823 K). The calcined sample was denoted TS-1-(Si/Ti)$^+$ or TS-2-(Si/Ti)$^+$. If not special specified, the Si/Ti in TS-1$^+$ and TS-2$^+$ was 82 and 54, respectively.

1.3 Post-treatment of TS-1 with TPAOH

As contrast, TS-1-TPAOH was post-treated as follows: TS-1-(Si/Ti) was suspended in an aqueous solution that contained TPAOH in a PTFE lining with molar composition of 1.0 SiO_2:0.04 TPAOH:10 H_2O, then the mixture was stirred for half an hour. The PTFE lining was put into a stainless-steel autoclave and crystallized at 443 K for 1 day. Then the product was recovered by filtration, drying, and calcinations (823 K). The calcined sample was denoted TS-1-(Si/Ti)-TPAOH.

2. Characterization methods

The X-ray diffraction (XRD) patterns were measured on a Rigaku Ultima IV diffractometer using Cu Kαradiation and a nickel filter in the 2 θ angle range from 5° to 35° at 35 kV and 25 mA. The UV−Visible diffuse reflectance spectra (UV/Vis) were recorded on a Shimadzu UV-2400PC spectrophotometer using $BaSO_4$ plate as a reference. Inductively coupled plasma (ICP) atomic emission spectroscopy was performed on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. Nitrogen physisorption was carried out on a BEL-MAX instrument at 77 K. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 microscope. Electron energy disperse spectroscopy (EDS, OXFORD INCA) and transmission electron microscopy (TEM) was taken on a JSM-2010F microscope. The infrared (IR) spectra were collected on Nicolet Nexus 670 FT-IR spectrometer at a spectral resolution of 2 cm^{-1}. For pyridine spectra measurement (1000-4000 cm^{-1}), it was recorded as follows: a self-supported wafer (9.6 mg/cm^{-1} thickness and 2 cm in diameter) was set in a quartz IR cell sealed with CaF_2 windows connected with a vacuum system. After the sample was evacuated at 723 K for 1 h, the pyridine adsorption was carried out by exposing the wafer to pyridine vapor (1.3 kPa) at 298 K for 20 min. The physisorbed and chemisorbed pyridine was then removed by evacuation at different temperatures (323 K-473 K) for 0.5 h. All the spectra were collected at room temperature. ^{29}Si solid-state MAS NMR spectra were recorded on a VARIAN VNMRS-400WB spectrometer under a one-pulse condition. The spectra were obtained with a frequency of 79.43 MHz, a spinning rate of 3000 rps, and a recycling delay of 60 s. The chemical shift was referred to Q8M8($[(CH_3)_3SiO]_8$-SiO_{12}). UV Raman spectra were recorded on UV-RAMAN100 Raman spectrometer made by Beijing ZOLIX INSTRUMENTS CO. LTD. A 244-nm line of a LEXEL laser of a He–Ge laser were used as the excitation sources. X-ray photoelectron spectra (XPS) were acquired with a Thermo Scientific ESCALAB250xi instrument using X-Ray Monochromatisation and operating at a constant power of 200 W. The obtained spectra were analyzed by a curve-fitting program XPSPEAK41.

3. Catalytic reactions

3.1 The epoxidation of alkene

The epoxidation of alkene was carried out at 333 K for 2 h in a 50 mL round-bottomed flask equipped with a reflux condenser. In a typical reaction, 50 mg of catalyst, 10 mL of CH_3OH, 10 mmol of alkene, and 10 mmol of H_2O_2 (30 wt % aqueous solution) under vigorous stirring. The product was analyzed on an Agilent GC-7890A gas chromatograph equipped with a DB-WAX capillary column (30 m × 320 μm × 0.25 μm) and an FID detector using cyclohexanone as an internal standard. The residual free H_2O_2 was determined by the titration method with 0.05 M $Ce(SO_4)_2$ solution.

3.2 The epoxidation of propylene

The epoxidation of propylene with H_2O_2 catalyzed by TS-1 samples was carried out in a stainless steel reactor that was immersed in a bath controlled at the required temperature. In a typical run, the mixture containing 100 mg of catalyst, 25 mL of solvent, 20 mmol of H_2O_2 aqueous solution (30 wt.%) were loaded into the reactor. Then propylene was charged at constant pressure (0.4 MPa) and the mixture was heated at 313 K under magnetic agitation for 1 h The reactive product was analyzed on an Agilent GC-7890A gas chromatograph equipped with a DB-WAX capillary column (30 m × 320 μm × 0.25 μm) by using 0.50 g of toluene as internal standard, and the unconverted H_2O_2 was calculated by titration with 0.05 M $Ce(SO_4)_2$ solution.

3.3 The continuous ammoximation of cyclohexanone

Continuous cyclohexanone ammoximation was carried out at 75^{o}C in a continuous slurry reactor (200 mL) with a condenser and a magnetic stirrer. In a typical run, TS-1 sample (3.2 g) was used as the catalyst. The mixture containing cyclohexanone, hydrogen peroxide, t-butyl alcohol and gas phase ammonia was continuously injected into the reactor using a plunger pump and a mass flow controller, respectively. The molar ratio of H_2O_2/ketone was 1.1:1. The molar ratio of NH_3/ketone was 1.7:1. Cyclohexanone was feeded at a rate of 81 g h^{-1}, WHSV (gram of cyclohexanone per hour per gram of catalyst) = 25.3 h^{-1}, respectively. The product was analyzed on an Agilent GC-7890A gas chromatograph equipped with a DB-WAX capillary column (30 m × 320 μm × 0.25 μm).

3.4 The activation of H_2O_2

The activation of H_2O_2 was carried out at 333 K for 2 h in a 50 mL round-bottomed flask equipped with a reflux condenser. In a typical reaction, 50 mg of catalyst, 10 mL of solvent, and 10 mmol of H_2O_2(30 wt % aqueous solution) under vigorous stirring. The residual free H_2O_2 was determined by the titration method with 0.05 M $Ce(SO_4)_2$ solution.

The detailed analysis on the formation mechanism of "TiO_6" species according to the characterization of ^{29}Si MAS NMR and XRD (Fig. 3).

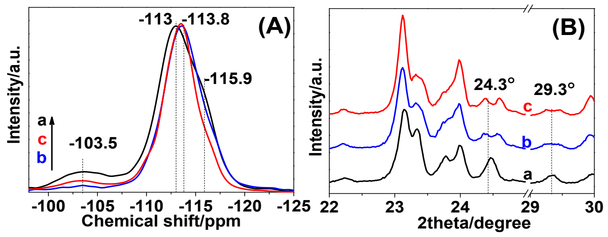

Fig. 3 ^{29}Si MAS NMR spectra (A) and XRD patterns (B) of TS-1 and S-1 samples (a) TS-1-82, (b) TS-1-82^+, (c) S-1.

As shown in Fig. 3Ac, with regard to S-1, a main peak at -113.8 ppm and a weak peak at -103 ppm appeared, which are assigned to $Si(OSi)_4$ (Q^4) featured with a perfect symmetry with Si-O-Si bands and $Si(OSi)_3OH$ (Q^3) species, respectively.[1] When Ti was introduced to synthesize TS-1 (Fig. 3Aa), a main peak of -113.0 ppm assigned to Q^4 had a 0.8 ppm shift to a higher field, and a new right shoulder peak of Q^4 appeared at -115.9 ppm, which resulted from the distortion of Si-O-Ti via the insertion of Ti leading to a less symmetry in Q^4.[1] However, after post-treatment, the main peak of Q^4 in TS-1^+ shifted back to low fields again with 0.8 ppm, appearing at -113.8 ppm just the same as S-1 (Fig. 3Ab). And the intensity of the right shoulder peak of Q^4 also reduced, which was more approximated to the Q^4 of S-1. This reveals that this post-treatment weakened the distortion extent of Si-O-Ti due to the generation of "TiO_6" species with double Ti-OH groups and water molecules. Furthermore, it is generally accepted that crystal system of MFI structure zeolite would change from the monoclinic to the orthogonal with insertion of Ti atoms, owing to the larger atomic radius of Ti than Si, and this difference in crystal system could be shown by the 2θ at 24.3° and 29.3° in the XRD patterns, in which monoclinic (S-1) displays double peaks in contrast to the single peak of orthogonal (TS-1).[2] Fig. 3B (a, c) also confirmed the obvious difference between S-1 and TS-1. However, after post-treatment, it is evident that two peaks appeared in 2θ at 24.3° and 29.3° in the XRD patterns of TS-1^+, which implies its crystal system was very similar to S-1 (Fig. 3B, b and c). These results intensely demonstrate that the removal of fractional Si species are adjacent to framework Ti sites, and the corresponding formed “TiO_6” units have less distortion effect on MFI structure, thus resulting in a more symmetrical structure similar to the monoclinic of S-1.

1 G. Ricchiardi, J. Sauer, *Zeitschrift für Physikalische Chemie*, 1999, **209**, 21.

2 M. Taramasso, G. Perego and B. Notari, *US Patent* 4410501, 1983.

Fig. S1 Ti 2p XPS spectra of TS-1 samples (a) TS-1-82, (b) TS-1-82$^+$

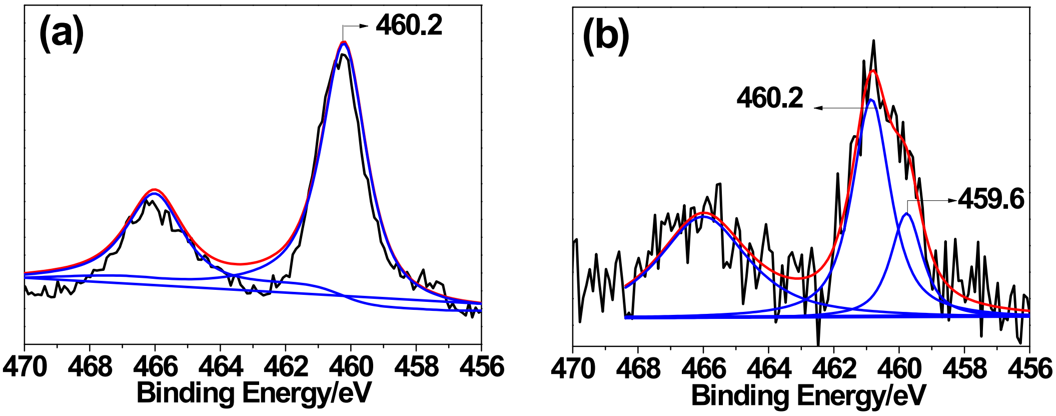

Fig. S2 FTIR spectra in the pyridine regions of TS-1-82 (A), TS-1-82$^+$ (B) at different evacuation temperatures; and the normalized area relative to Lewis acid sites (1445 cm^{-1}) vs evacuation temperatures (C).

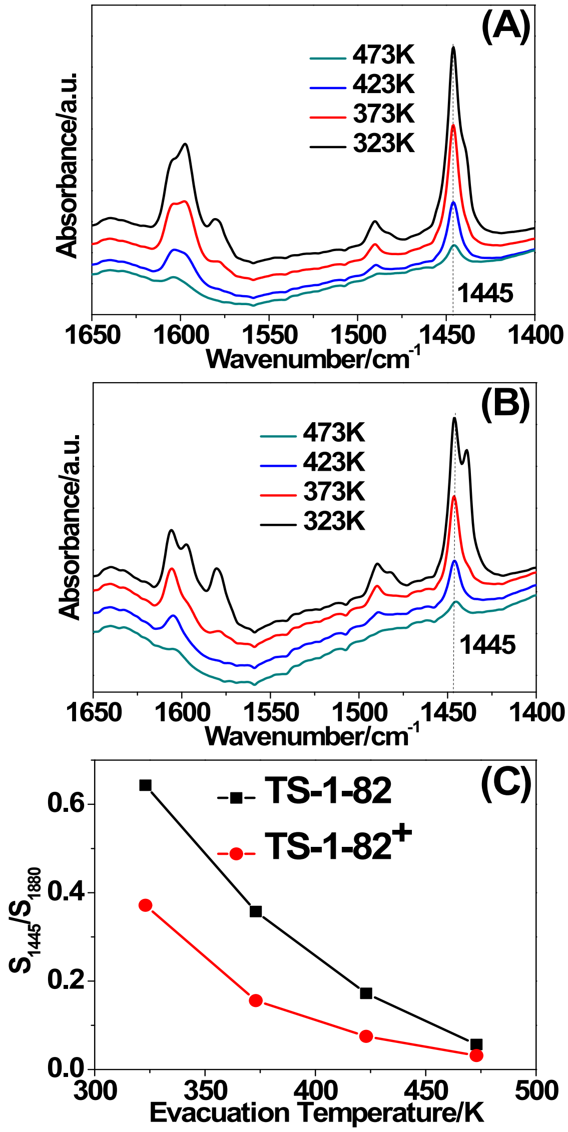

Fig. S3 The SEM images of parent TS-1-82 (a) and TS-1-82$^+$ (b, c, d, e) with prolonged hydrothermal treatment times (b) 2 h, (c) 4 h, (d) 6 h, (e) 24 h.

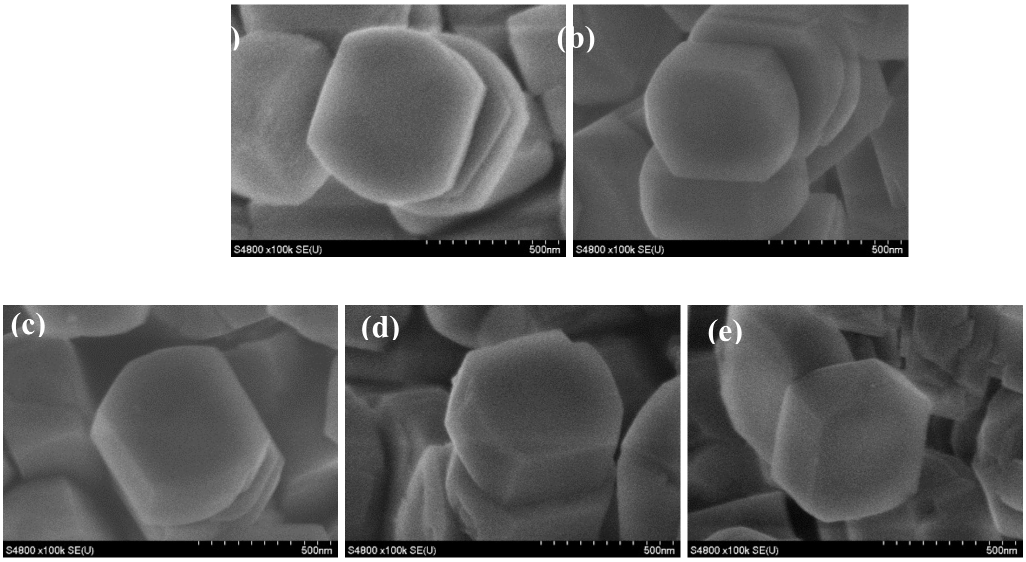

Fig. S4 TEM images of TS-1-82, TS-1-82$^+$ and corresponding EDS line scans.

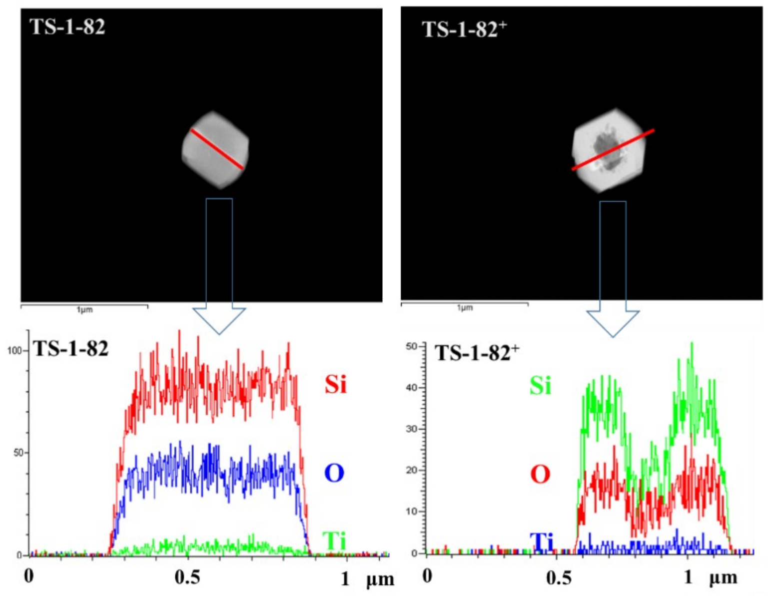

Fig. S5 XRD patterns of TS-1 samples (a) TS-1-82, (b) TS-1-82$^+$.

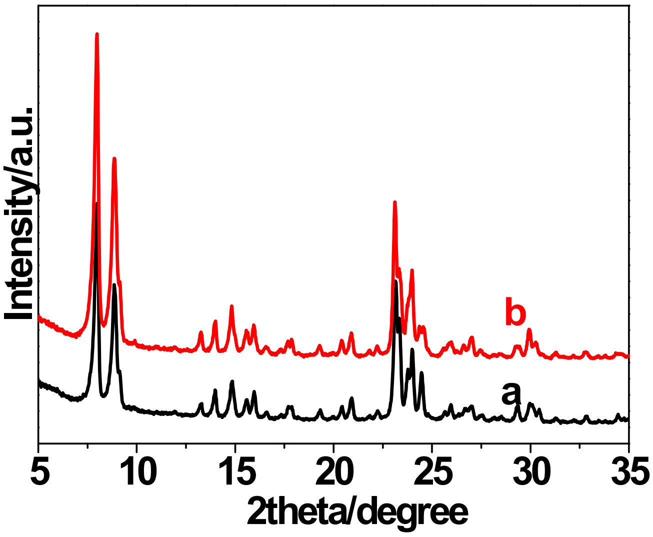

Fig. S6 UV/Vis spectra of TS-1$^+$ samples (Si/Ti = 82) over varying synthesis conditions (A) crystallization temperature, (B) crystallization time.

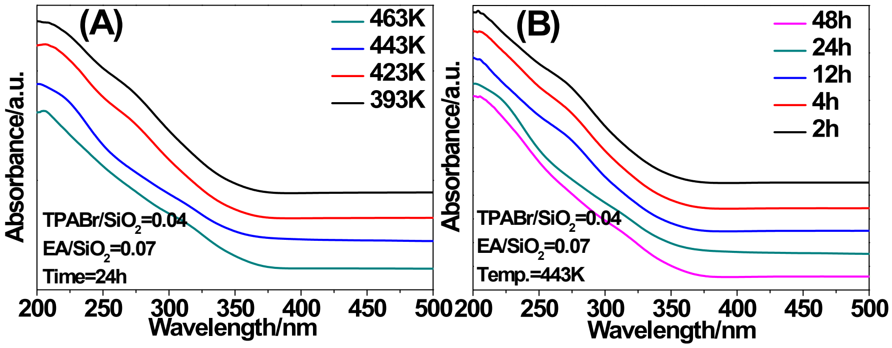

Fig. S7 The epoxidation of 1-hexene over TS-1 and TS-1^+ samples over varying synthesis conditions (A) TPABr/SiO_2, (B) EA/SiO_2, (C) crystallization temperature, (D) crystallization time

Reaction conditions: catalyst 50 mg (Si/Ti=82), 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3OH 10 ml, temp. 333 K, time 2 h.

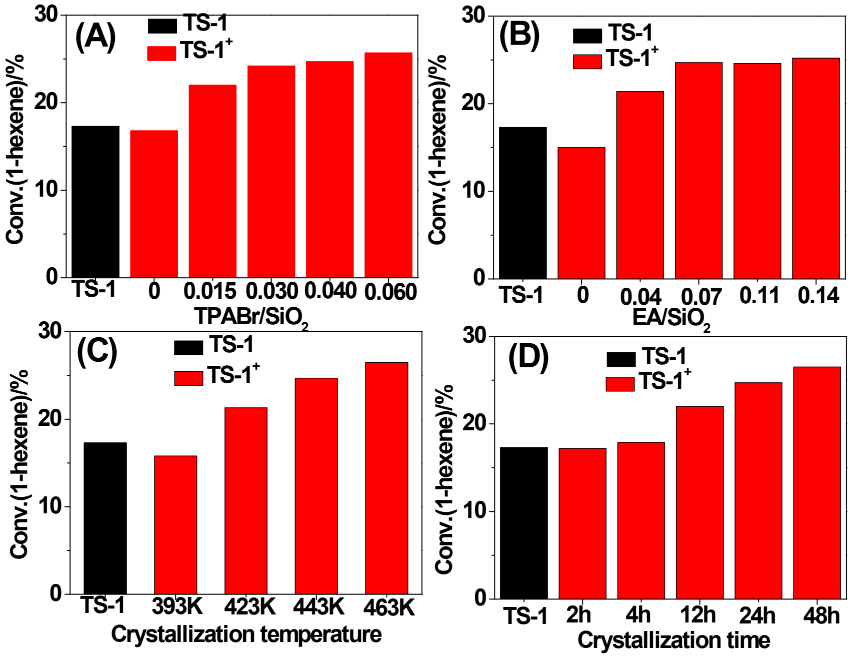

Fig. S8 Epoxidation of different alkenes over TS-1-82 and TS-1-82$^+$

Reaction conditions: catalyst 50 mg, substrates 10 mmol, H_2O_2 10 mmol, CH_3OH 10 ml, temp. 333 K, time 2 h.

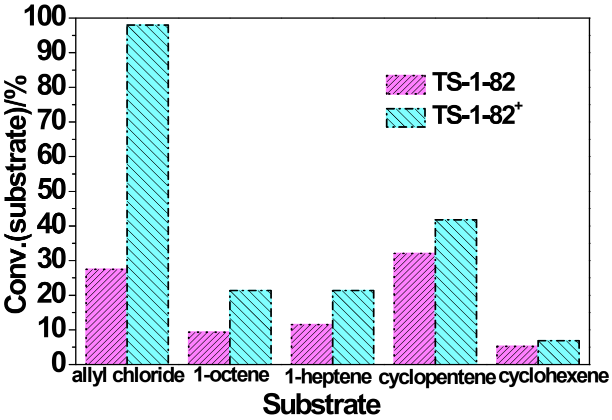

Fig. S9 The ability of activating H_2O_2 over TS-1 and TS-1^+ in various Ti contents. Reaction conditions: catalyst 50 mg, H_2O_2 10 mmol, CH_3OH 10 ml, temp. 333 K, time 2 h.

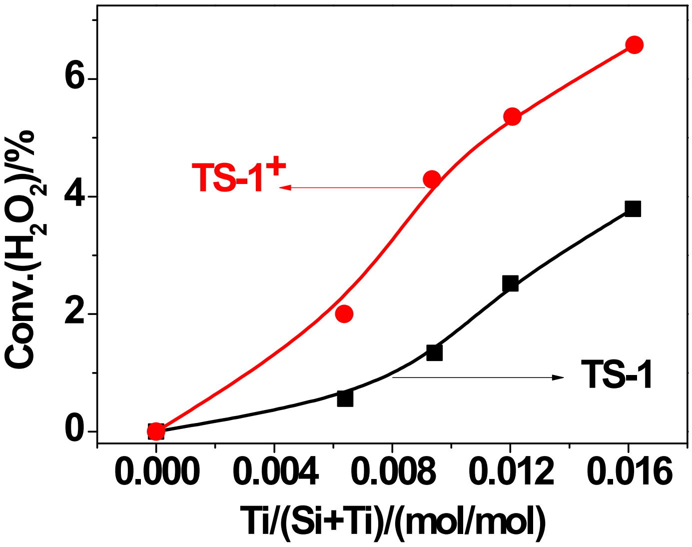

Fig. S10 A comparison of lifetime of continuous ammoximation of cyclohexanone catalyzed by TS-1 samples.

Reaction conditions: NH_3/cyclohexanone 1.7, H_2O_2/cyclohexanone 1.1, temp. 348 K.

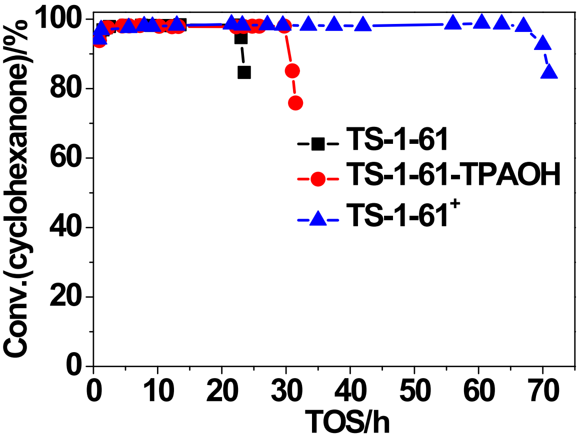

Table S1 Quantify of Ti with different states in 1-hexene epoxidation over TS-1 and TS-1$^+$ samples

No.	Sample	PEAK-1/%[a]	PEAK-2/%[a]	PEAK-3/%[a]	TON(PEAK-1)[b]	TON(PEAK-2)[b]
1	TS-1-61	100	0	0	188	
2	TS-1-61$^+$	82.01	17.99	0	188	498
3	TS-1-82	100	0	0	173	
4	TS-1-82$^+$	80.86	19.14	0	173	551
5	TS-1-105	100	0	0	189	
6	TS-1-105$^+$	76.98	23.02	0	189	540
7	TS-1-157	100	0	0	172	
8	TS-1-157$^+$	75.80	24.20	0	172	419

[a] PEAK from the area of different peaks in UV-Vis spectra (PEAK-1, 210nm; PEAK-2, 260~290nm; PEAK-3, 330nm). [b] TON in mol (mol of Ti)$^{-1}$, turnover number per Ti site for 1-hexene conversion.

Table S2 Epoxidation of propylene with H_2O_2 over TS-1 samples[a]

No.	Samples	Yield(PO)/ %	Conv.(H_2O_2)/ %	Sel.(PO)/ %	Eff[b].(H_2O_2)/ %
1	TS-1-82	48.9	61.2	97.8	83.1
2	TS-1-82-TPAOH	49.0	60.7	98.4	83.6
3	TS-1-82$^+$	76.4	98.7	92.8	80.5
4	TS-1-82^{+c}	79.3	99.0	98.5	83.3

[a] Reaction conditions: catalyst 100 mg, CH_3OH 25 mL, propylene pressure 0.4 MPa, H_2O_2 (30 wt%) 20 mmol, temp. 313 K, time 1 h. [b] Efficiency of H_2O_2 = (amount of products/amount of H_2O_2 consumed) × 100. [c] A small of $NH_3 \cdot H_2O$ was added.

Table S3 Epoxidation of 1-hexene with H_2O_2 over TS-2-54 and TS-2-54^{+a}

No.	Sample	1-hexene Conv.(%)	H_2O_2 Conv.(%)	Oxide Sel.(%)	H_2O_2 Eff.[b] (%)
1	TS-2-54	6.7	9.2	100	73.2
2	TS-2-54$^+$	17.7	22.0	90.2	80.5

[a] Reaction conditions: catalyst, 50 mg; CH_3OH, 10 mL; 1-hexene,10 mmol; H_2O_2 (30 wt%), 10 mmol; temperature, 333 K; time, 2 h. [b] Efficiency of H_2O_2 = (amount of products/amount of H_2O_2 consumed) × 100.