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Facile synthesis of a high-performance titanosilicate catalyst with controllable defective Ti(OSi)$_3$OH sites

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Catalyst preparation

Synthesis of TS-1: TS-1 was hydrothermally synthesized following the literature[1]. A typical synthesis of TS-1 in a two-step hydrolysis method is as follows. In the first step, a mixture of all TBOT and partial TEOS 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:(0.015-0.030) 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: (0.0076-0.015) 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 76.

Synthesis of TS-2: TS-2 (Si/Ti = 54) was prepared according to the literature[2].

Synthesis of TS-1$^+$: TS-1$^+$ (Si/Ti = 76) was prepared according to the literature[3].

Synthesis of TS-1-TPAOH: TS-1-TPAOH (Si/Ti = 76) was prepared according to the literature[4].

Synthesis of TS-1^s and TS-2^s: In a typical run, TS-1-(Si/Ti) or TS-2-(Si/Ti) was suspended in an aqueous solution that contained organic amine in a PTFE lining, the typical aqueous solution has the following molar composition: 1.0 SiO_2: 0.07 amine: 8 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 containing amine/SiO_2 (0.02-0.35), crystallization time (2-48 h), crystallization temperature (393-463 K) and organic amine type (Methanamine (MA), Ethylamine (EA), n-Propylamine (nPA), n-Butylamine (nBA) et al) 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)^s or TS-2-(Si/Ti)^s. If not special specified, the Si/Ti in TS-1^s and TS-2^s was 76 and 54, respectively.

Catalyst characterization

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 and Electron energy disperse spectroscopy (EDS) were taken on a Hitachi S-4800 microscope., OXFORD INCA. 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 $mg \cdot cm^{-1}$ 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 and ^{1}H solid-state MAS NMR spectra were recorded on a VARIAN VNMRS-400WB spectrometer under a one-pulse condition. ^{29}Si MAS NMR was 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}). And ^1H MAS NMR spectra was obtained with a frequency of 400.1 MHz, a spinning rate of 10000 rps, the chemical shift was referred to TMS($(CH3)_4Si$). 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.

Catalytic reaction

The epoxidation of 1-hexene 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 1-hexene, 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.

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.

Continuous cyclohexanone ammoximation was carried out at 348 K 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).

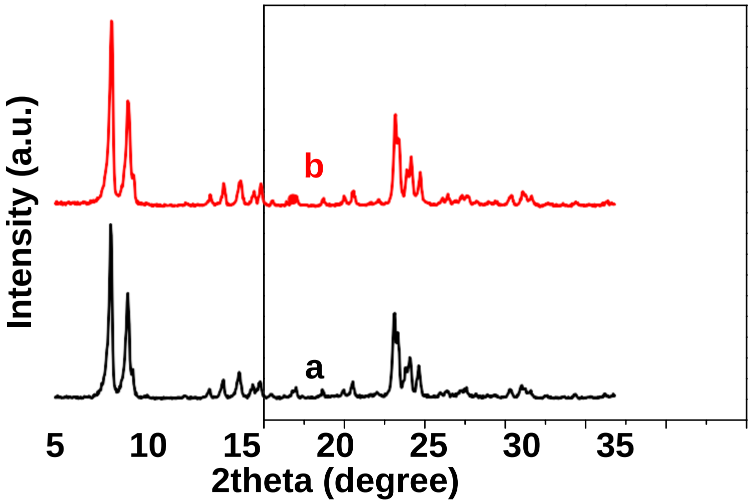

Figure. S1 The XRD patterns of TS-1-76 (a) and TS-1-76^{s} (b) samples

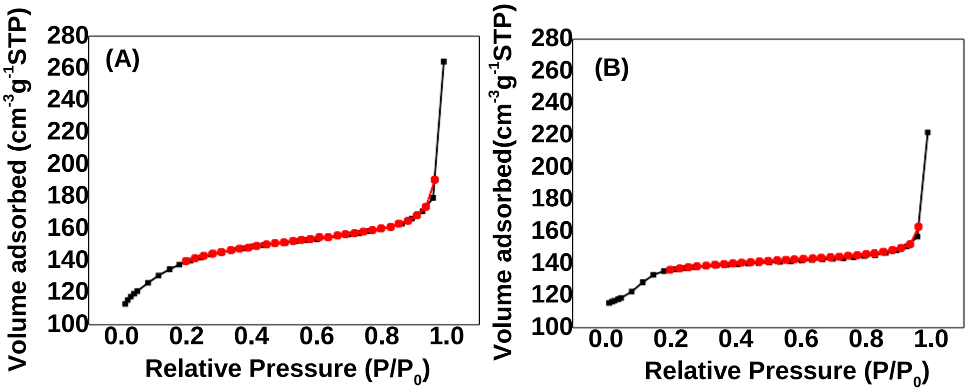

Fig. S2 N_2 adsorption-desorption isotherms of TS-1-76 (A) and TS-1-76^S (B)

Table S1 Physicochemical properties of TS-1 samples

No.	Sample	Si/Ti[a]	Smicro[b]	Sexter[b]	Vmicro[b]	Vmeso[b]
1	TS-1	76	398	98	0.175	0.105
2	TS-1^s	76	392	95	0.173	0.093
3	TS-1-76-TPAOH[c]	76	387	93	0.172	0.387

[a]. Detected by ICP . [b] Calculated by BET method. S_{micro}($m^2 \cdot g^{-1}$), S_{exter}($m^2 \cdot g^{-1}$), V_{micro}($cm^3 \cdot g^{-1}$) and V_{meso}($cm^3 \cdot g^{-1}$) stand for microporous surface area, external surface area, microporous volume and mesoporous volume, respectively. [c]TS-1-76 was hydrothermal treated by TPAOH.

Table S2 The atomic charge and corresponding Ti-O bonds length in $Ti(OSi)_4$ and $Ti(OSi)_3OH$ active sites

	Atomic charge[a]					Ti-O bonds length (Å)[a]			
	Ti	O1	O2	O3	O4	Ti-O1	Ti-O2	Ti-O3	Ti-O4
$Ti(OSi)_4$	+1.189	-0.681	-0.648	-0.681	-0.695	1.77764	1.75572	1.77769	1.77676
$Ti(OSi)_3OH$	+1.267	-0.664	-0.694	-0.690	-0.724	1.77887	1.75681	1.78277	1.83942

[a] Optimized Structural Parameters of the Ti sites Model Calculated at the B3LYP/6-31G(d).

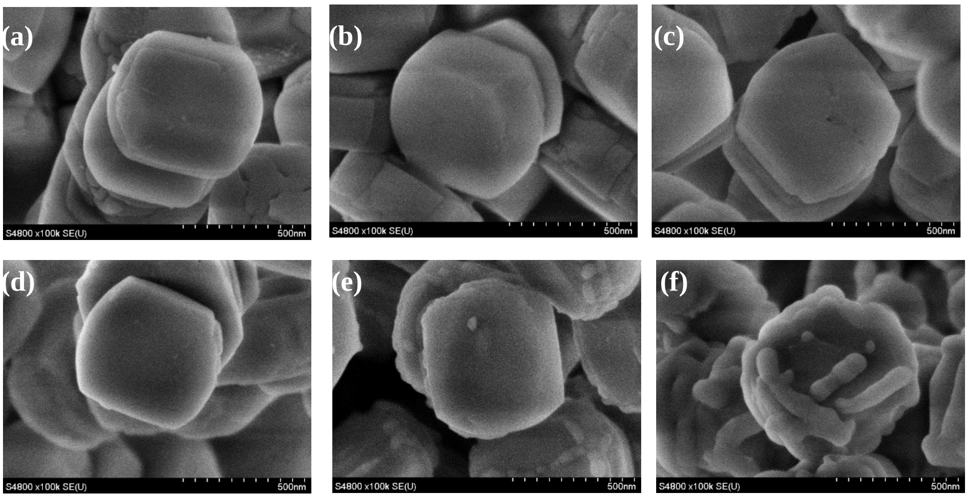

Fig.S3 The SEM images of parent TS-1-76 (a) and TS-1-76^s (b, c, d, e, f) with prolonged hydrothermal treatment times (b) 2 h, (c) 6 h, (d) 12 h, (e) 24 h, (f) 48 h.

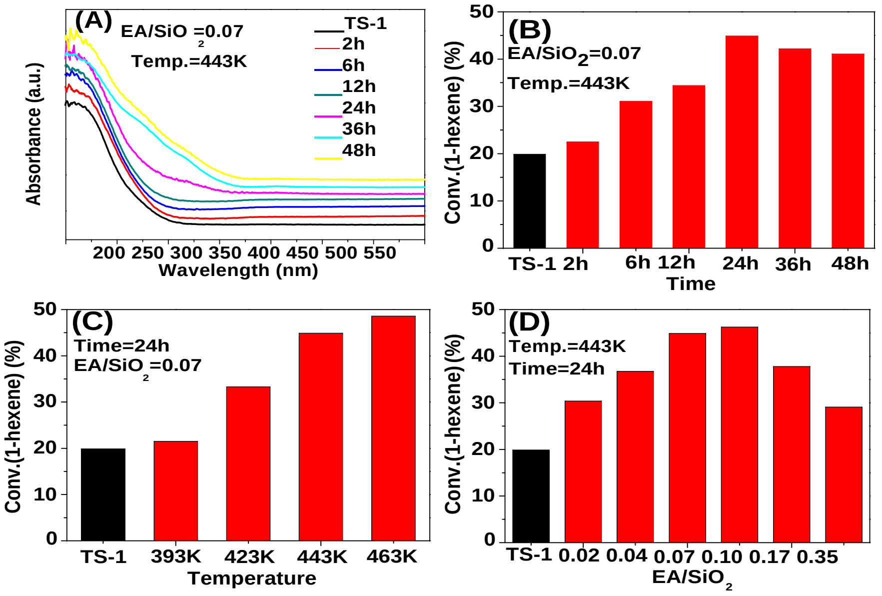

Fig.S4 The UV-Vis spectra and corresponding 1-hexene epoxidation activity of TS-1^s with different preparation conditions. (A) The UV-Vis spectra of hydrothermal treatment time (2-48 h); (B) The corresponding 1-hexene epoxidation activity of (A); (C) (D) The 1-hexene epoxidation activity of the hydrothermal treatment temperature (393-463 K) and the ratio of EA/SiO$_2$ (0.02-0.14). Reactions conditions: catalyst 50 mg, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3OH 10 mL, temp. 333 K, time 2 h

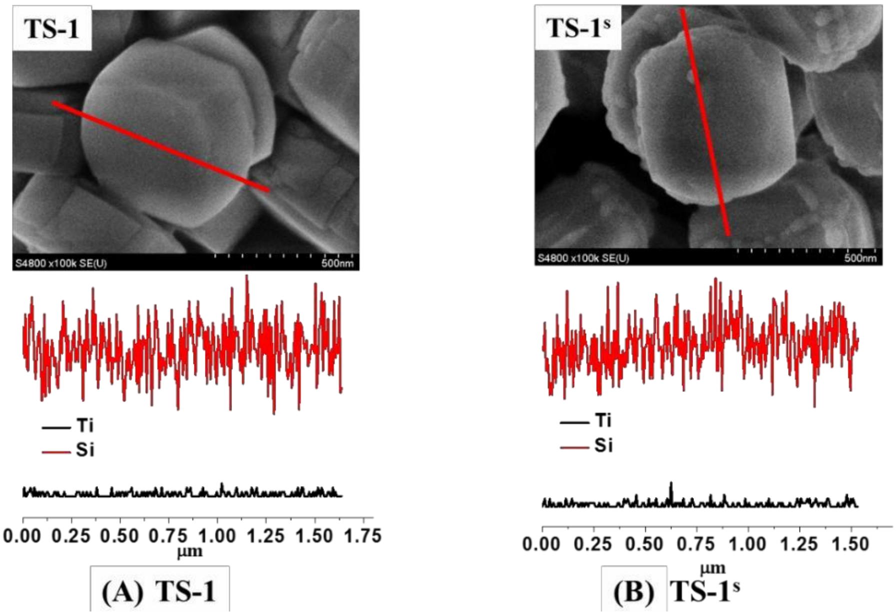

Fig. S5 SEM images of TS-1-76 (A), TS-1-76^s (B) and corresponding EDS line scans.

Table S3 Elemental composition of TS-1 samples

No.	Samples	Si/Ti(Bulk)[a]	Si/Ti(Surface)[b]
1	TS-1	76	138
2	TS-1^{s}(24h)	76	75

[a] Detected by ICP; [b] Detected by XPS

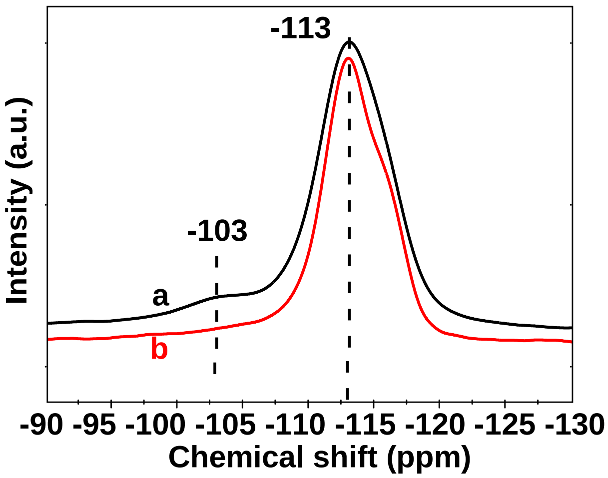

Fig. S6 ^{29}Si MAS NMR spectra of TS-1-76 (a) and TS-1-76^{s} (b) samples

Table S4 The different amines to synthesize TS-1^s and corresponding 1-hexene epoxidation activity

No.	Samples	Amines[a]	Si/Ti[b]	Conv. (1-hex.) (mol%)	Conv.(H_2O_2) (mol%)	Eff.(H_2O_2) (%)	Sel.(Epo.) (mol%)
1	TS-1	/	76	19.9	27.8	71.6	94.3
2	TS-1^s	MA	76	34.9	43.1	81.0	95.2
3	TS-1^s	EA	76	44.9	57.2	78.5	94.0
4	TS-1^s	*n*PA	76	34.5	44.0	78.4	92.7
5	TS-1^s	*n*BA	76	30.0	36.8	81.7	92.4
6	TS-1	TPAOH	76	20.2	24.6	82.0	100
8	TS-2	EA	54	6.6	9.0	73.3	100
9	TS-2^s	EA	54	14.9	17.5	84.8	90.6

[a] No.2-No.6, TS-1 was hydrothermal treated by MA, EA, nPA, nBA and TPAOH, respectively.

[b] Detected by ICP.

Reactions conditions: catalyst 50 mg, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3OH 10 mL, temp. 333 K, time 2 h

Table. S5 Quantify of Ti with different states and corresponding TON in 1-hexene epoxidation over TS-1 and TS-1^s samples

No.	Samples	Peak-1 (%)[a]	Peak-2 (%)[a]	Peak-3 (%)[a]	TON (Peak-1)[b]	TON (Peak-2)[b]	TON (Peak-3)[b]
1	TS-1-76	100	0	0	184	/	/
2	TS-1-76^s	66	34	0	184	864	/
3	TS-1-76$^+$	75	0	25	184	/	535
3	TS-1-100	100	0	0	186	/	/
4	TS-1-100^s	50.5	49.5	0	186	685	/
5	TS-1-131	100	0	0	178	/	/
6	TS-1-131^s	44.1	55.9	0	178	644	/

[a] Peak from the area of different peaks in UV-Vis spectra (Peak-1, 205 nm; Peak-2, 235 nm; Peak-3, 330 nm).

[b] TON in mol (mol of Ti)$^{-1}$, turnover number per Ti site for 1-hexene conversion

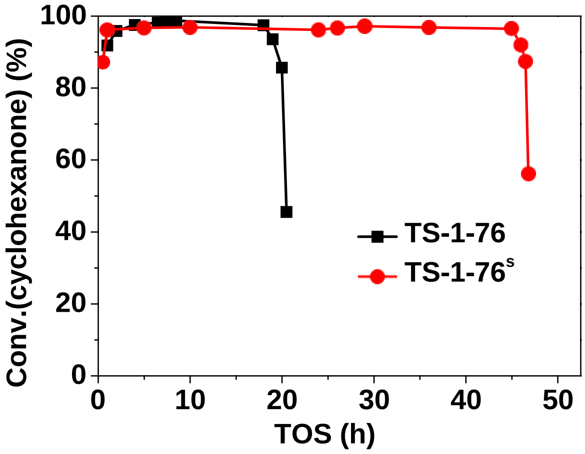

Fig. S7 A comparison of lifetime of continuous ammoximation of cyclohexanone catalyzed by TS-1 samples. Reaction conditions: NH_3/cyclohexanone 1.7, H_2O_2/cyclohexanone 1.1, temp. 348 K.

Table S6 Epoxidation of propylene with H_2O_2 over TS-1 samples[a]

No.	Samples	Yield(PO) (mol%)	Conv.(H_2O_2) (mol%)	Sel.(PO) (mol%)	Eff.(H_2O_2) (%)
1	TS-1-76	49.2	61.4	95.8	80.1
2	TS-1-76^s	82.2	97.2	93.6	84.5

[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.

Reference

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