Electronic Supplementary Information (ESI)

One-step rapid synthesis of TS-1 zeolites with highly catalytic active mononuclear TiO_6 species

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Chemicals and materials

The reagents used in this work include tetraethylorthosilicate (TEOS, Shanghai Chemical Reagent), tetrabutyl orthotitanate (TBOT, Shanghai Chemical Reagent), tetrapropylammonium hydroxide (25 wt%, Guangfu Fine Chemical Research Institute), H_2O_2 (30 wt%, Beijing Chemical Works), 1-hexene (98%, Aladdin), methanol (99%, Guangfu Fine Chemical Research Institute), ethanol (99%, Guangfu Fine Chemical Research Institute), and chlorobenzene (99%, DaMao Chemical Reagent Factory).

Characterizations

The crystallinity and phase purity of the samples were characterized by power X-ray diffraction (XRD) on a Rigaku D- Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å) . The crystal size and morphology were measured by a scanning electron microscopy (SEM) using a JSM-6700F (JEOL) electron microscope. Transmission electron microscopy (TEM) images were recorded with a Tecnai F20 electron microscope. Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77 K after degassing the samples at 623 K under vacuum. Chemical compositions were determined with an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS). Infrared spectra (IR) were recorded by Nicolet Impact 410 FT-IR Infrared Instrument using KBr pellet technique. The UV-Vis DRS (diffuse reflectance spectroscopy) of the catalyst was recorded over the range of 200 nm to 500 nm against the support as reference, on a SHIMADZU U-4100. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. Ultraviolet Raman resonance spectroscopy (UV-Raman) (266 nm) were recorded on a DL-2 Raman spectrometer using the 266 nm line of a He-Ge laser as the excitation source and a Princeton CCD as the detector. X-ray absorption spectroscopy data were collected at the Sector 20-BM beamline of the Advanced Photon Source at Argonne National Laboratory. Sample powders were packed on plastic washer and folded multiple times to enhance the signal. The beamline was equipped with a double-crystal Si (111) monochromator. A 12-element Ge fluorescence detector was used to collect spectra of the Ti K-edge. Data processing and EXAFS fitting were performed using the Athena, Artemis and Igor software.

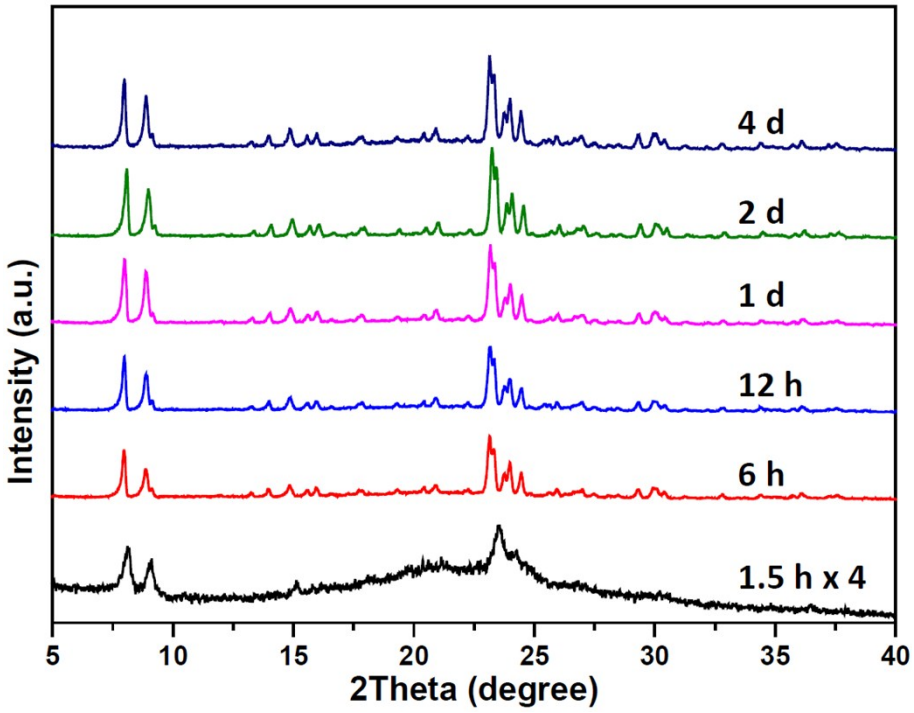

Fig. S1 XRD patterns of conventional TS-1 zeolites of different crystallization time.

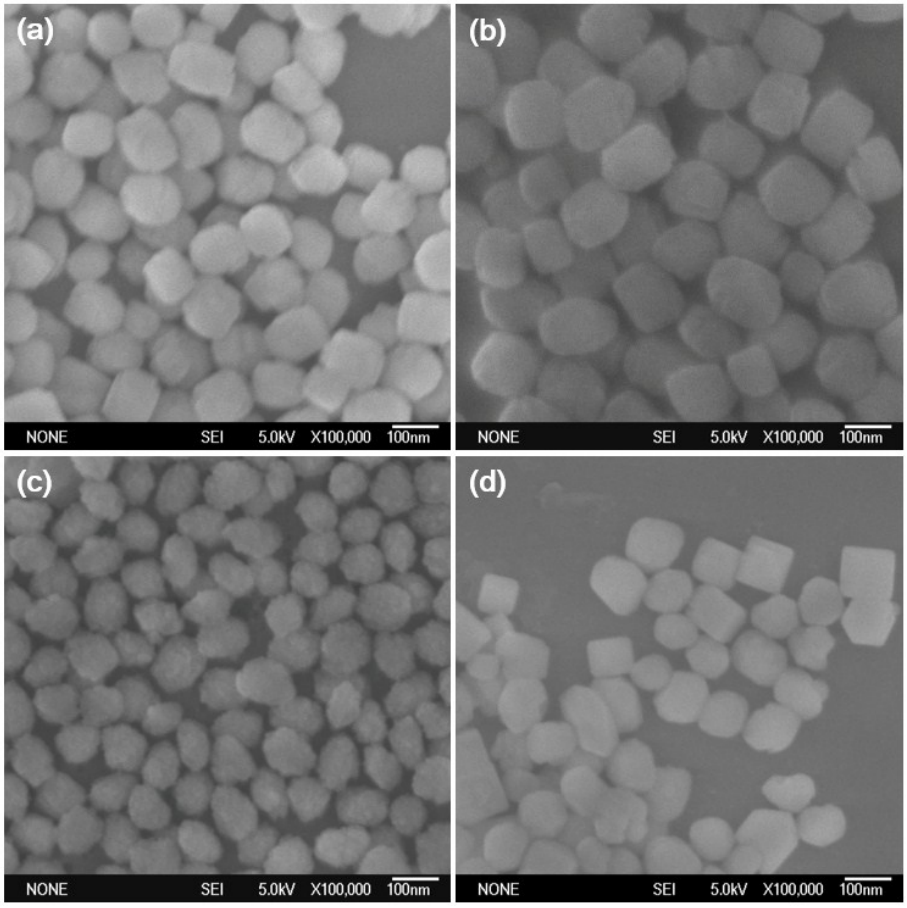

Fig. S2 SEM images of conventional TS-1 (TS-1-C) (a), active seeds-assisted microwave irradiation TS-1 (TS-1-AM) (b), active seeds-assisted TS-1 (TS-1-A) (c), microwave-assisted TS-1 (TS-1-M) (d) zeolites.

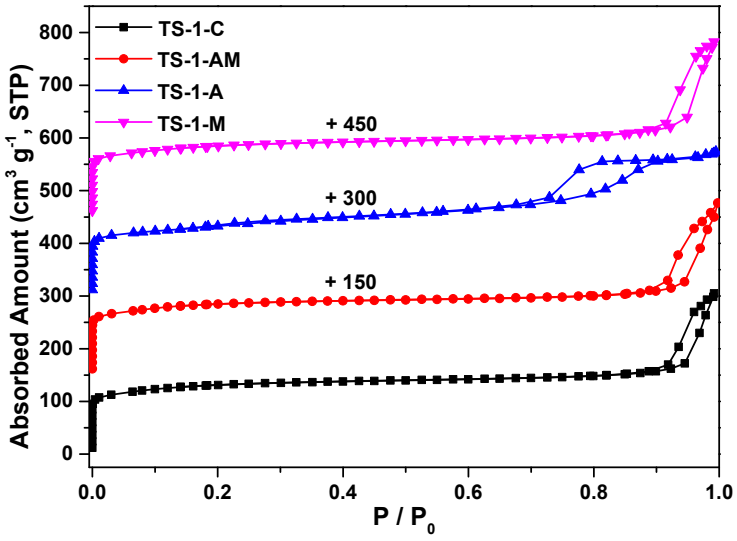

Fig. S3 N_2 adsorption–desorption isotherms of different TS-1 zeolites.

Table S1 textural properties of different TS-1 zeolites.

samples	**S_{BET} (m^2/g)[a]**	**S_{micro} (m^2/g)[b]**	**S_{ext} (m^2/g)[b]**	**V_{micro} (cm^3/g)[b]**
TS-1-C	439.1	271.9	167.2	0.13
TS-1-AM	451.2	280.9	170.3	0.13
TS-1-A	449.8	234.9	214.9	0.11
TS-1-M	452.5	272.5	180.0	0.13

a. S_{BET} (total surface area) calculated using the BET method; b. S_{micro} (micropore area), S_{ext} (external surface area) and V_{micro} (micropore volume) calculated using the t-plot method.

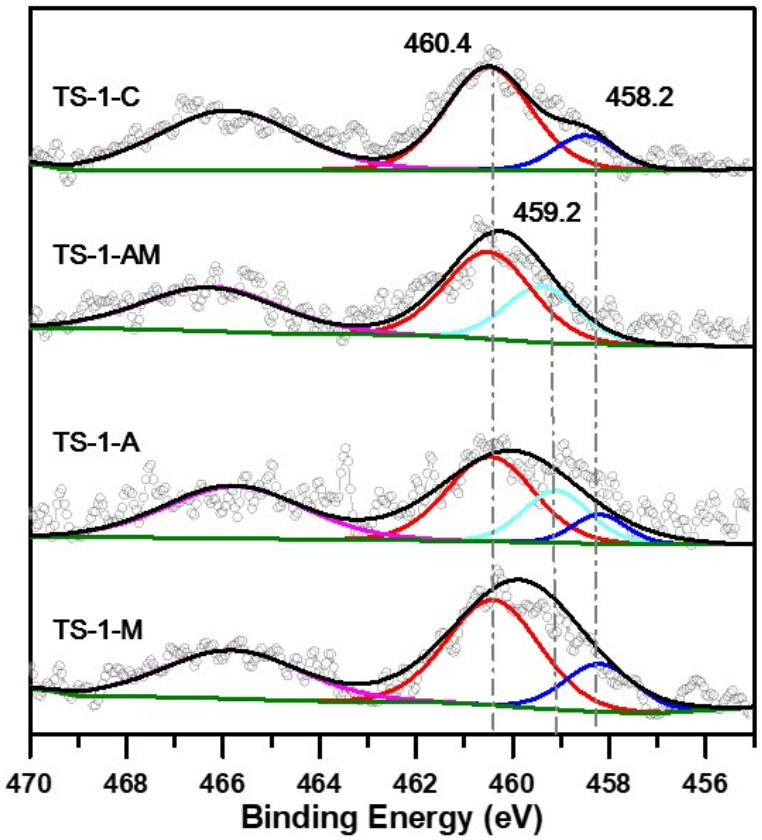

Fig. S4 XPS spectra of TS-1-C, TS-1-AM, TS-1-A, TS-1-M zeolites.

The XPS spectra of the Ti 2p region are presented in Fig. S4. The peaks at 460.4, 459.2 and 458.2 eV should be attributed to framework TiO_4, high coordinated Ti species and anatase TiO_2, respectively.[1-2]

1. L. Z. Wu, X. J. Deng, S. F. Zhao, H. M. Yin, Z. X. Zhuo, X. Q. Fang, Y. M. Liu and M. Y. He, *Chem. Commun.*, 2016, **52**, 8679-8682.

2. A. C. Alba-Rubio, J. L. G. Fierro, L. León-Reina, R. Mariscal, J. A. Dumesic, M. López. Granados, *Appl. Catal., B*, 2017, **202**, 269-280.

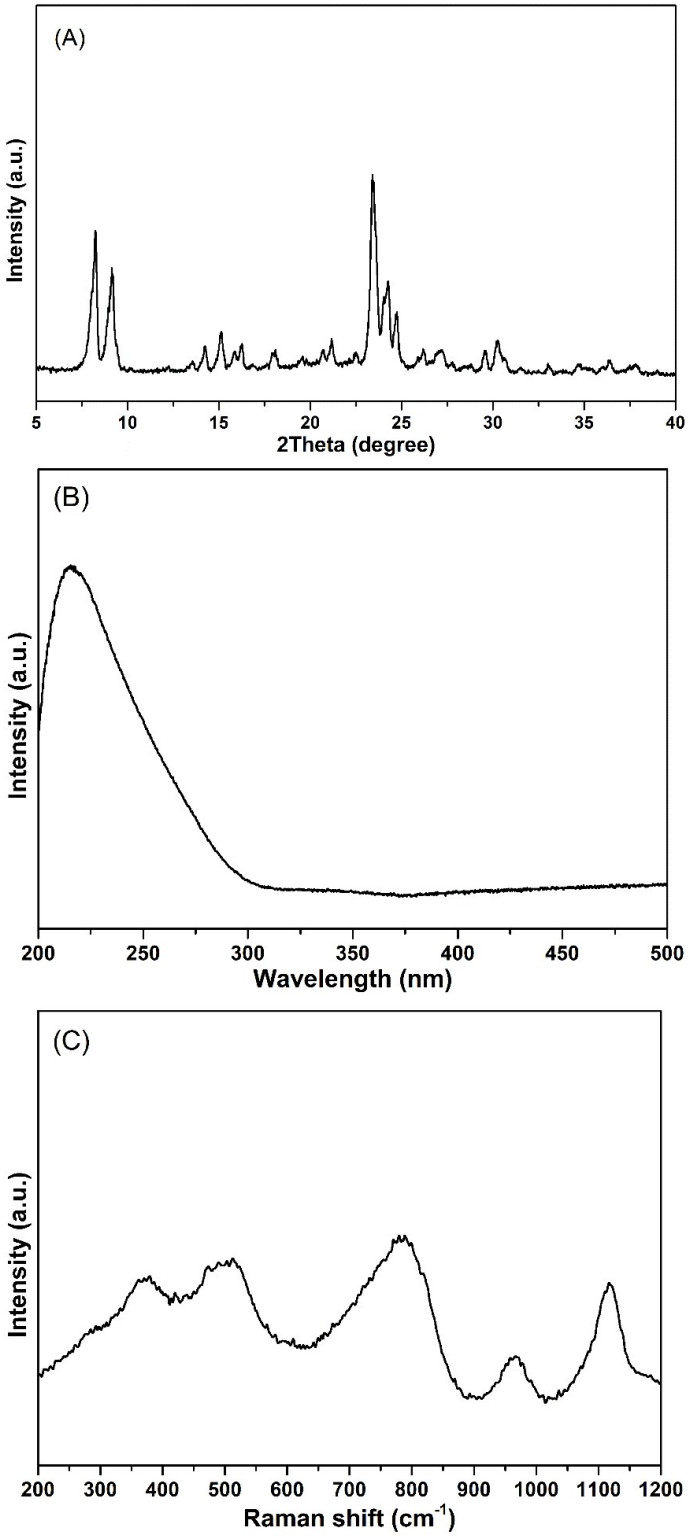

Fig. S5 The XRD patterns (A), UV-vis (B) and UV-Raman (C) spectra of TS-1-TiO_4 zeolite.

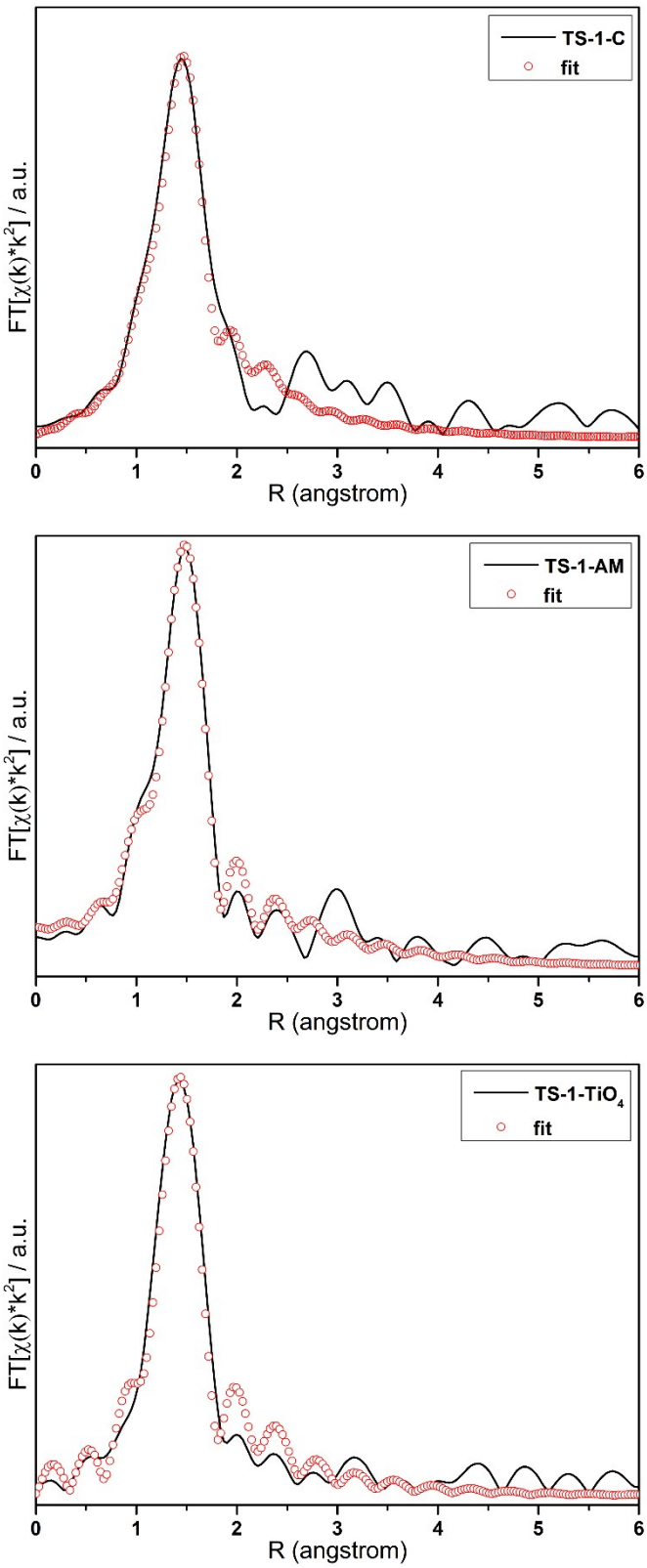

Figure S6. Experimental data (solid black lines) and fits (empty red circles) of Fourier-transformed Ti K edge EXAFS spectra for different TS-1 zeolites.

Table S2. Structural parameters of different TS-1 zeolites extracted from the EXAFS fitting.

Sample	Shell	C.N.	R (Å)	σ (Å^2)	ΔE_0 (eV)	R-factor (%)
TS-1-C	Ti-O	4.5(8)	1.84(2)	0.004(3)	5.2(3)	2.4
TS-1-AM	Ti-O	4.3(6)	1.83(1)	0.001(1)	9.6(3)	0.9
TS-1-TiO_4	Ti-O	4	1.82(1)	0.0004(1)	6.8(2)	2.2

C.N. is the coordination number; R is bond distance; σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero-kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

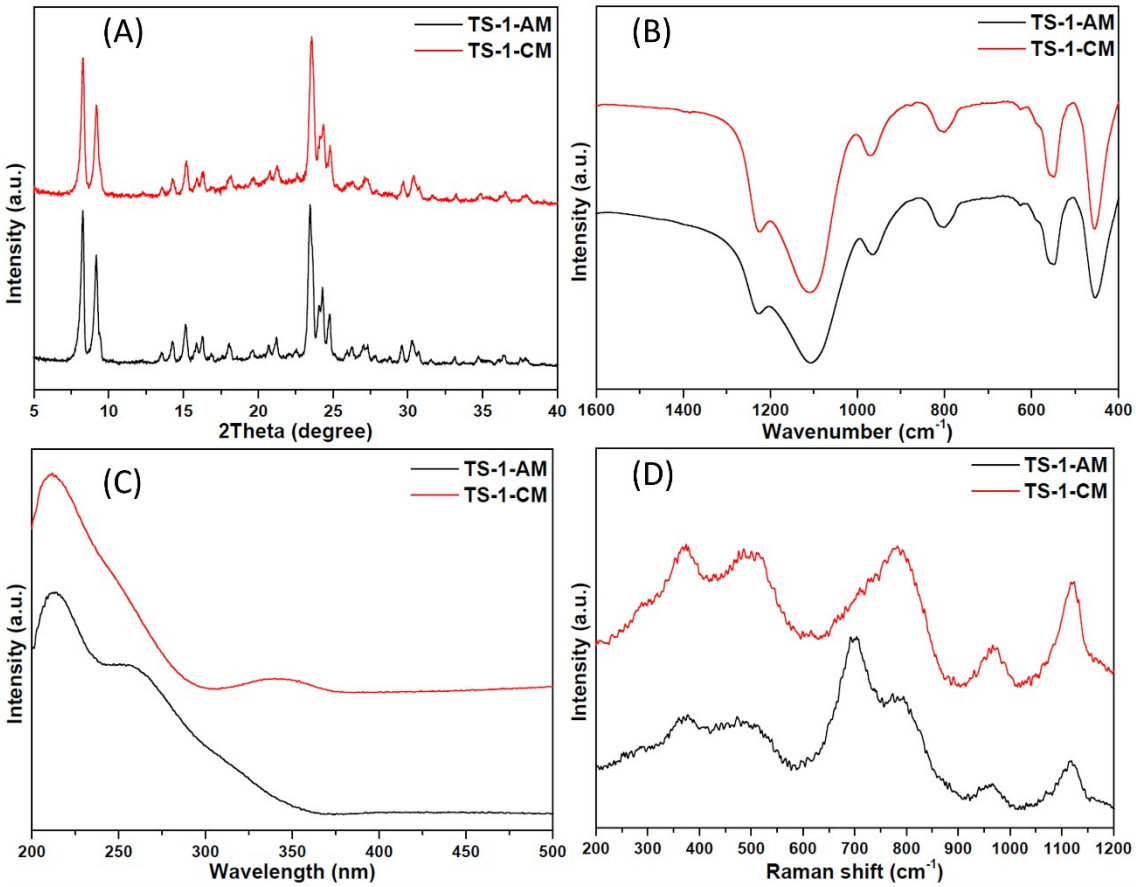

Fig. S7 The XRD patterns (A), UV-vis (B), FTIR (C) and UV-Raman (D) spectra of TS-1-AM and TS-1-CM zeolites.

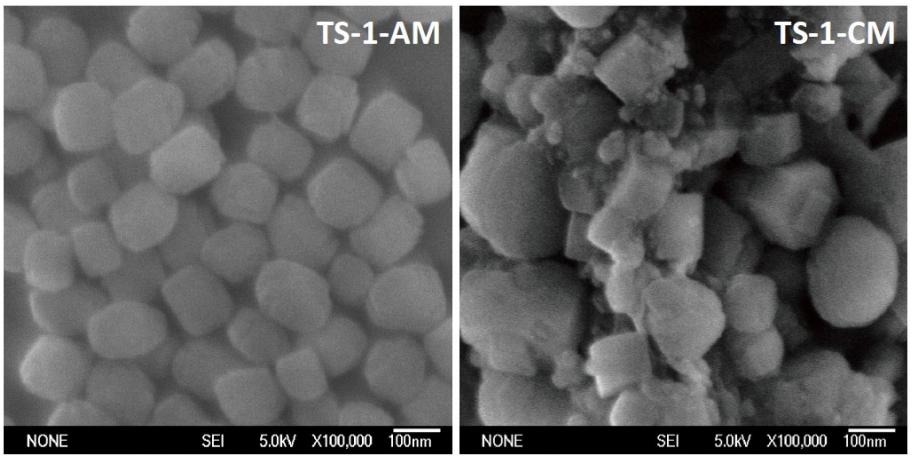

Fig. S8 The SEM images of TS-1-AM and TS-1-CM zeolites.

Table S3 Epoxidation of 1-hexene over different TS-1 catalysts

	$I_{960/800}$	Si/Ti[a]	Conv. (%)	Sel. (%)		TON[b]
				epoxide	others	
TS-1-AM	1.10	80	28.0	90.0	10.0	272
TS-1-CM	1.13	71	20.1	90.1	9.9	177

a. The elemental compositions are determined by XRF; b. TON in mol (mol of Ti)$^{-1}$, turnover number per Ti site for 1-hexene conversion. Reaction conditions: catalyst 50 mg, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3OH 10 mL, temp. 333 K, time 2 h. Others, 1-methoxyhexan-2-ol, 2-methoxyhexan-1-ol, 1,2-hexanediol.

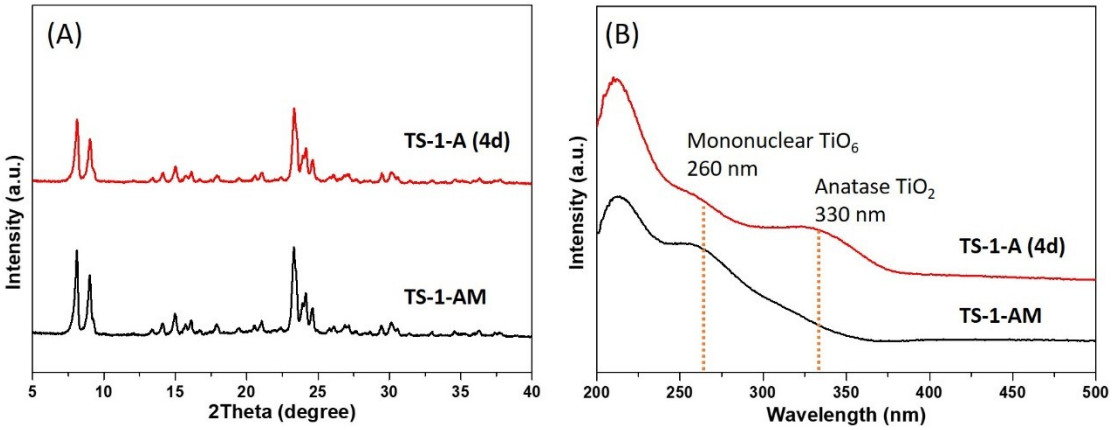

Fig. S9 The XRD patterns (A) and UV-vis (B) spectra of TS-1-AM and TS-1-A (4d).

Table S4 Epoxidation of 1-hexene over different TS-1 catalysts

	Si/Ti[a]	Conv. (%)	Sel. (%)		TON[b]
			epoxide	others	
TS-1-AM	80	28.0	90.0	10.0	272
TS-1-TiO_4	90	16.5	95.6	4.4	181
TS-1-A (4d)	69	18.6	92.4	7.6	156

a. The elemental compositions are determined by XRF; b. TON in mol (mol of Ti)$^{-1}$, turnover number per Ti site for 1-hexene conversion. Reaction conditions: catalyst 50 mg, 1-hexene 10 mmol, H_2O_2 10 mmol, CH_3OH 10 mL, temp. 333 K, time 2 h. Others, 1-methoxyhexan-2-ol, 2-methoxyhexan-1-ol, 1,2-hexanediol.

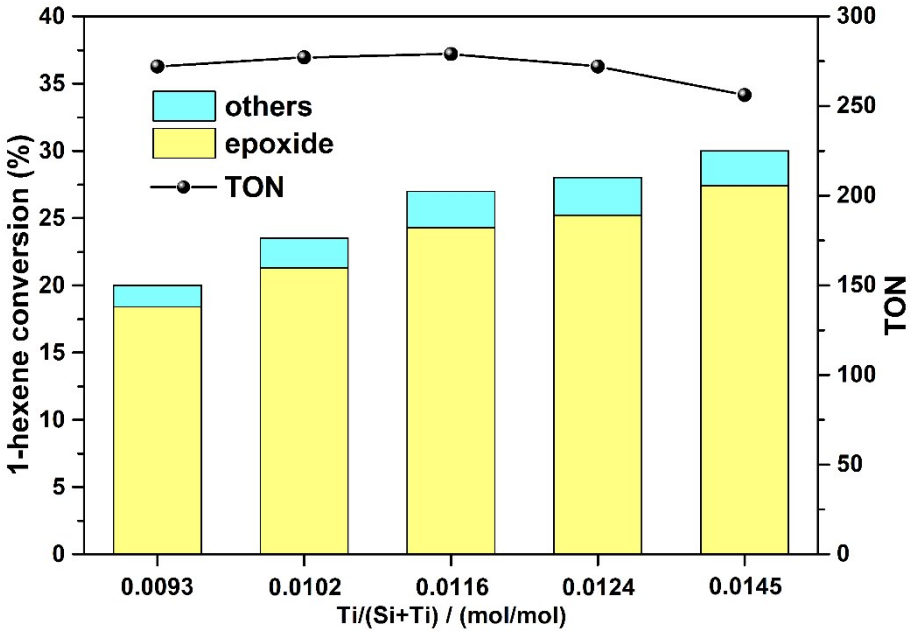

Fig. S10 Epoxidation of 1-hexene over TS-1-AM with various Ti contents.

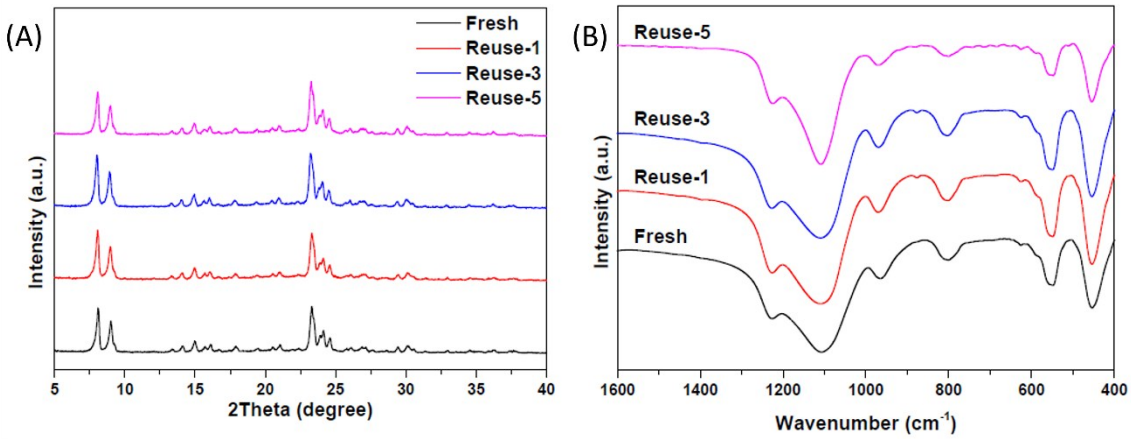

Fig. S11 The XRD patterns (A) and FT-IR (B) spectra of TS-1-AM in reuse test.