# **Supplementary Information**

# Crystallization-controlled microstructure of titanium species in TS-1 zeolite for tailored catalytic performance

Siqi Chen,<sup>a</sup> Jingxuan Wang,<sup>a</sup> Tianjun Zhang,<sup>b</sup> and Risheng Bai<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

<sup>b</sup> College of Chemistry and Materials Science, Hebei University, Baoding, 071002, P.R. China.

\*Corresponding Author: Risheng Bai (rsbai@jlu.edu.cn)

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# Experimental

#### **Reactant agents**

All reagents were used as purchased commercially without any further purification. Tetrapropylammonium hydroxide (TPAOH) (40 wt%, Kent), tetrabutyl titanate (TBOT, 98%, Macklin), tetraethyl orthosilicate (TEOS, 99%, Adamas), dibenzothiophene (DBT, 98%, Macklin), tert-butyl hydroperoxide solution (70 wt%, Macklin), 1-hexene (99%, Macklin), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30 wt%, Aladdin).

### **Preparation of TS-1 zeolites**

The TS-1 zeolites were prepared with the following molar composition: 1.0 SiO<sub>2</sub>: 0.0256 TiO<sub>2</sub>: 0.388 TPAOH: 6.25 H<sub>2</sub>O under static hydrothermal conditions (170 °C), with tetrapropylammonium hydroxide (TPAOH) as the organic structure directing agent and with tetrabutyl titanate (TBOT) as the Ti source. Typical synthesis procedure is as follows: mixing TPAOH (40 wt%) with distilled water, add TBOT and stir for 1 h. Afterward, add tetraethyl orthosilicate (TEOS) into the system and stir for 12 h to get the complete hydrolysis. Then introduce the synthesis gel into a Teflon-lined stainless-steel autoclave. Crystallization is carried out at 170 °C under static conditions for different crystallization times. After centrifugation, the products were washed sequentially with water and ethanol, then dried and calcined at 550 °C for 8 h under an air atmosphere to remove the organic template.

# Characterizations

# X-ray diffraction (XRD)

Powder X-ray diffraction analysis (PXRD) of the samples was carried out on Malvern panalytical Empyrean High Throughput XRD using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å, 50 KV).

# Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were recorded on JEOL JEM-2100F and Talos F200s electron microscope.

# Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were recorded on JEOL JSM-7800F electron microscope.

## Nitrogen physisorption

Nitrogen adsorption-desorption measurements were carried out on a BSD-660M A6MB6M analyzer at 77.3 K. Before starting the  $N_2$  adsorption measurements, all the samples were activated by degassing in-situ at about 573 K for 10 h.

### Inductively coupled plasma (ICP)

Chemical compositions were determined with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis performed on an iCAP 7000 SERIES.

# Thermogravimetric Analysis (TGA)

Thermalgravimetric (TG) analyses were performed using NETZSCH STA449F3 QMS403D and Bruker V70 at temperatures ranging from room temperature to 700 °C at a heating rate of 10 °Cmin<sup>-1</sup>.

#### X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 X-ray photoelectron spectrometer using Al as the excitation source.

### Fourier transform infrared spectra (FT-IR)

The Fourier Transform Infrared Spectrometer (FT-IR) were recorded on a Bruker VERTEX 80v, samples were pelleted with KBr powder before testing.

#### **Ultraviolet Visible absorption spectroscopy (UV-Vis)**

The Ultraviolet Visible absorption spectroscopy (UV-Vis) of the catalysts was recorded over the range of 200 nm to 500 nm against the support as reference, on a HITACHI U-4100.

#### Solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR)

The <sup>1</sup>H and <sup>29</sup>Si solid-state MAS NMR experiments were performed at 14.09 T on a Bruker Avance Neo 600WB spectrometer at resonance frequencies of 600.23 and 119.24 MHz, respectively, with a magic angle spinning rate of 8 kHz. Single-pulse <sup>1</sup>H MAS NMR experiments were performed using a  $\pi/2$  <sup>1</sup>H pulse length of 4.0 µs, a repetition time of 2 s, and 32 scans. For the two-dimensional (2D) <sup>1</sup>H-<sup>1</sup>H double quantum (DQ) single quantum (SQ) MAS NMR measurements, DQ coherences were excited and reconverted with a POST-C7 pulse sequence.<sup>1</sup> The increment interval in the indirect dimension was 80 µs. Typically, 128 scans were acquired for each t<sub>1</sub> increment, and two-dimensional data sets consisted of 128 t<sub>1</sub> × 256 t<sub>2</sub>. The <sup>1</sup>H MAS NMR signals were referenced to adamantane (1.82 ppm).

Single-pulse <sup>29</sup>Si MAS NMR spectra with high power proton decoupling were recorded on a 3.2 mm probe, using a  $\pi/2$  pulse of 5.1 µs, a recycle delay of 80 s and 128 scans.

#### X-ray absorption spectroscopy (XAS)

The data of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were collected at room temperature in the fluorescent mode with a Lytle detector at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF, China). The samples were measured in fluorescence mode, using a Lytle detector to collect the data. Data processing and EXAFS fitting were performed using the Athena, Artemis and Igor software.

# Catalytic tests

#### Oxidative desulfurization of Dibenzothiophene (DBT).

A model fuel with a sulfur concentration of about 500 ppm was prepared by dissolving DBT in n-octane. The oxidative desulfurization reaction was performed in a 50 mL three-necked round-bottom flask, connected to a reflux cooler system with magnetic stirring. The catalyst was activated at 473 K for 2 h before used. Typically, 30 mg catalyst was added into 7 g of model fuel, then 25 mg n-Hexadecane and 28.2 mg of TBHP were added in turn, which acted as internal standard and oxidant, respectively. The reaction was carried at 343 K for 15 min under magnetic stirring of 1200 rpm to eliminate the effects of the external mass transfer resistances of the catalysts. The products were analyzed by gas chromatography (Huifen GC7800 System) equipped with HP-5 column (Agilent 30 m  $\times$  320  $\mu$ m  $\times$  0.1  $\mu$ m) and FID detector and gas chromatography mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with TG-5MS column, L=60 m). Mass balances were accurate to within 5%.

#### **Epoxidation of 1-hexene.**

The epoxidation of 1-hexene with  $H_2O_2$  as oxidant, n-dodecane as internal standard, and methanol as the solvent was carried out in batch reactors. The catalyst was activated at 473 K for 2 h before used. In a typical run, 1-hexene (10 mmol),  $H_2O_2$  (10 mmol), catalyst (50 mg), and methanol (10 mL) were added into the batch reactor. The reaction was carried at 333 K under magnetic stirring of 800 rpm. Sample analyses were performed on a gas chromatography (Huifen GC7800 System) equipped with HP-5 column (Agilent 30 m × 320  $\mu$ m × 0.1  $\mu$ m). Mass balances were accurate to within 5%.

The activation energy *Ea*, is calculated from the Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

Where: *k* is the observed rate constant; *A* is the pre-exponential factor; *Ea* is the activation energy (J mol<sup>-1</sup>); *R* is the universal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>); and *T* is the temperature (K).

Supplementary figures and tables



Figure S1. (a) PXRD patterns and (b) relative crystallization of synthesized samples.



Figure S2. TG curves of synthesized samples.



Figure S3. FT-IR spectra of synthesized samples.



Figure S4. (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distributions of synthesized samples.



Figure S5. SEM images of (a-c) TS-1-Amor-4H, (d-f) TS-1-Semi-8H, (g-i) TS-1-Semi-12H and (j-l) TS-1-Cryst-24H.



**Figure S6.** TEM images of (a, b) TS-1-Amor-4H, (c, d) TS-1-Semi-8H, (e, f) TS-1-Cryst-12H and (g, h) TS-1-Cryst-24H samples.



Figure S7. FFT images of different areas in TS-1-Semi-8H.



**Figure S8.** (a) <sup>29</sup>Si MAS NMR spectra and (b) <sup>1</sup>H MAS NMR spectra of TS-1-Amor-2H and TS-1-Cryst-48H.



Figure S9. Photos of initial synthetic mixtures with different crystallization time.



**Figure S10.** Experimental data (solid lines) and fits (empty circles) of Fourier transformed Ti K edge EXAFS spectra for (a) TS-1-Amor-2H and (b) TS-1-Cryst-48H.



**Figure S11.** PXRD patterns of fresh TS-1-Amor-2H and used TS-1-Amor-2H after 5 cycles of DBT oxidation.



Figure S12. UV-vis spectra of fresh TS-1-Amor-2H and used TS-1-Amor-2H after 5 cycles of DBT oxidation.



Figure S13. FT-IR spectra of fresh TS-1-Amor-2H and used TS-1-Amor-2H after 5 cycles of DBT oxidation.



Figure S14. Reusability in DBT oxidation over TS-1-Cryst-48H.



Figure S15. PXRD patterns of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of DBT oxidation.



Figure S16. UV-vis spectra of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of DBT oxidation.



Figure S17. FT-IR spectra of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of DBT oxidation.



Figure S18. PXRD patterns of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of the epoxidation of 1-hexene.



**Figure S19.** UV-vis spectra of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of the epoxidation of 1-hexene.



**Figure S20.** FT-IR spectra of fresh TS-1-Cryst-48H and used TS-1-Cryst-48H after 5 cycles of the epoxidation of 1-hexene.

Sample	S <sub>BET</sub>	Smicro	S <sub>ext</sub>	V <sub>total</sub>	Vmicro	V <sub>meso</sub>	Si/Ti <sup>f</sup>	Si/Ti <sup>g</sup>
	$(m^2/g)^a$	$(m^2/g)^b$	$(m^{2}/g)^{b}$	(cm <sup>3</sup> /g) <sup>c</sup>	(cm <sup>3</sup> /g) <sup>d</sup>	(cm <sup>3</sup> /g) <sup>e</sup>		
TS-1-Amor-2H	832	128	704	1.13	0.05	1.08	38.6	27.7
TS-1-Amor-4H	620	197	423	1.56	0.08	1.48	34.4	31.8
TS-1-Semi-8H	583	258	325	1.75	0.11	1.64	35.4	35.4
TS-1-Cryst-12H	466	389	77	0.44	0.16	0.28	35.9	34.4
TS-1-Cryst-24H	500	418	82	0.65	0.18	0.47	36.9	33.5
TS-1-Cryst-48H	475	426	49	0.38	0.19	0.19	36.9	31.8

Table S1. Textural properties of synthesized TS-1 samples.

<sup>a</sup> Surface area was calculated from the nitrogen adsorption isotherm using the BET method.

<sup>b</sup> S<sub>micro</sub> (micropore area), S<sub>ext</sub> (external surface area) were calculated using the t-plot method.

<sup>c</sup>  $V_{total}$  (total pore volume) at  $P/P_0 = 0.99$ .

<sup>d</sup> V<sub>micro</sub> (micropore volume) was calculated using the t-plot method.

 $^{e}$  V<sub>meso</sub> (mesopore volume) = V<sub>total</sub> (total pore volume) - V<sub>micro</sub>.

<sup>f</sup> Measured by inductively coupled plasma (ICP).

<sup>g</sup> Measured by X-ray photoelectron spectroscopy (XPS).

Sample	Shell	C.N. <sup>a</sup>	R (Å) <sup>b</sup>	$R(\mathring{A})^b \qquad \sigma(\mathring{A}^2)^c$		R-factor
					(ev) <sup>a</sup>	(%)
TS-1-Amor-2H	Ti-O	$4.8 \pm$	$1.83\pm0.01$	$0.0017 \pm 0.0015$	$-4.7\pm1.5$	1.3
		0.6				
TS-1-Cryst-48H	Ti-O	$4.4 \pm$	$1.80\pm0.02$	$0.0018 \pm 0.0022$	$6.7\pm2.1$	2.1
		0.7				

 Table S2. Structural parameters of TS-1-Amor-2H and TS-1-Cryst-48H samples extracted from

 the EXAES fitting

<sup>a</sup> C.N. is the coordination number.

<sup>b</sup> R is bond distance.

 $^{c}\sigma^{2}$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances).

 ${}^{d}\Delta E_{0}$  is edge energy shift (the difference between the zero-kinetic energy value of the sample and that of the theoretical model).

<sup>e</sup>R factor is used to value the goodness of the fitting.

Sample	Mass of	Temp.	Reaction	Removal of	
-	catalyst (mg)	(K)	time (min)	DBT (%)	Ref.
TS-1-Amor-2H	30	343	15	100	This work
TS-1-Cryst-48H	30	343	15	59.7	This work
TS-1(H1)	55	333	15	100	Ref.S2
TS-1(H3)	55	333	15	100	Ref.S2
TS-1(C3)	55	333	15	60.7	Ref.S2
AM-TS-0	80	333	10	48.0	Ref.S3
AM-TS-95	80	333	10	100	Ref.S3
AM-TS-130	80	333	10	100	Ref.S3
MTS-PTS	50	333	30	92.8	Ref.S4
MTS-HU2	50	333	30	100	Ref.S4
TS-1A	50	333	15	68.1	Ref.S5
TS-1B	50	333	15	70.0	Ref.S5
TS-1C	50	333	15	73.1	Ref.S5
TS-1-h	50	333	360	62.0	Ref.S6
TS-1-d	50	333	360	99.0	Ref.S6
HTS-1-50	50	333	30	100	Ref.S7
TS-1-50-CP	50	333	30	94	Ref.S7

 Table S3. Comparison of catalytic performance over synthesized samples and some representative

 TS-1 catalysts in oxidation desulfurization of DBT

Sample	Mass of Temp. Reaction Vield of Sel. of					
~ mpro	catalyst (mg)	(K)	time (h)	epoxide (%)	epoxide (%)	Ref.
TS-1-Cryst-48H	50	333	2	25.9ª	>99	This work
MTS-PTS	50	333	2	29.4 <sup>b</sup>	96.2 <sup>b</sup>	Ref.S4
MTS-PM	50	333	2	26.4 <sup>b</sup>	96.9 <sup>b</sup>	Ref.S4
MTS-HU1	50	333	2	32.6 <sup>b</sup>	97.3 <sup>b</sup>	Ref.S4
MTS-HU2	50	333	2	34.2 <sup>b</sup>	98.4 <sup>b</sup>	Ref.S4
MTS-HU3	50	333	2	29.9 <sup>b</sup>	96.2 <sup>b</sup>	Ref.S4
TS-1-AM	50	333	2	25.2 <sup>b</sup>	90.0 <sup>b</sup>	Ref.S8
TS-1-C	50	333	2	17.5 <sup>b</sup>	93.2 <sup>b</sup>	Ref.S8
TS-1-A	50	333	2	11.6 <sup>b</sup>	94.7 <sup>b</sup>	Ref.S8
TS-1-M	50	333	2	11.5 <sup>b</sup>	94.5 <sup>b</sup>	Ref.S8
TS-1-NC1	100	333	2	60.5 <sup>b</sup>	80.4 <sup>b</sup>	Ref.S9
TS-1-C1	100	333	2	51.7 <sup>b</sup>	74.9 <sup>b</sup>	Ref.S9
TS-1-NC1-sil	100	333	2	60.5 <sup>b</sup>	81.6 <sup>b</sup>	Ref.S9
TS-1-C1-sil	100	333	2	43.9 <sup>b</sup>	74.7 <sup>b</sup>	Ref.S9
TS-1-NC2-S	100	333	2	8.7 <sup>b</sup>	>99 <sup>b</sup>	Ref.S9
TS-1-C2-S	100	333	2	6.8 <sup>b</sup>	>99 <sup>b</sup>	Ref.S9
TS-1-3.5P	50	333	2	40.0 <sup>b</sup>	97.9 <sup>b</sup>	Ref.S10
TS-1-10.5P	50	333	2	46.8 <sup>b</sup>	97.7 <sup>b</sup>	Ref.S10
TS-1-17.5P	50	333	2	31.8 <sup>b</sup>	97.1 <sup>b</sup>	Ref.S10
TS-1-P	50	333	2	23.0 <sup>b</sup>	97.0 <sup>b</sup>	Ref.S11
TS-1-P-am	50	333	2	26.1 <sup>b</sup>	97.4 <sup>b</sup>	Ref.S11
TS-1-PN	50	333	2	28.1 <sup>b</sup>	98.1 <sup>b</sup>	Ref.S11
TS-1-PN-am	50	333	2	34.8 <sup>b</sup>	98.2 <sup>b</sup>	Ref.S11

 Table S4. Comparison of catalytic performance over synthesized samples and some representative

 TS-1 catalysts in epoxidation of 1-hexene.

<sup>a</sup> Yield of epoxide is calculated by the mole ratio of n(produced 1,2-epoxyhexene)/n(initial 1-hexene).

<sup>b</sup> Calculated by the data from the references.

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