

Regulation of TS-1 Zeolite Morphology by Crystallization Modifiers to Boost the Oxidative Reactions

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Experimental section

Chemicals

Tetrapropylammonium hydroxide solution (TPAOH; 25 wt%), dibenzothiophene (DBT; 99 %): Innochem Science & Technology. Tetraethyl orthosilicate (TEOS; 98%), tetrabutyl orthotitanate (TBOT; 98%): Sinopharm. *N,N*-Dimethylformamide (DMF; 99.5%), *N,N*-dimethylacetamide (DMA; 99.5%): Tianjin Tiantai fine chemicals co., ltd. Methanol (99.5%), n-octane (97 %): Tianjin Fuchen Chemical Reagent Factory. Tert-butyl hydroperoxide solution (TBHP; 70 wt%): Alfa Aesar (China) Chemicals. H₂O₂ (30 wt%): Beijing Chemical Works. 1-hexene (98%), n-dodecane (99.7%), *N,N*-Dimethylpropionamide (DMP; 99%): Aladdin. All of these materials were utilized without additional purification processes.

Synthesis of catalysts

Syntheses of TS-1-DMF, TS-1-DMA and TS-1-DMP samples.

TS-1 zeolite (MFI type) was synthesized via hydrothermal method with a molar composition of SiO₂: 0.020 TiO₂: 0.28 TPAOH: 28 H₂O: 0.27 CGM (CGM represents DMF, DMA or DMP). In a typical procedure, TPAOH was dissolved in water with stirring, followed by dropwise addition of TEOS. After complete hydrolysis, TBOT was added dropwise, and the mixture was stirred for a few hours. CGMs were then added and stirred for 24 hours. The reaction gel was crystallized at 80 °C for 3 hours and then at 120 °C for 96 hours under static conditions in Teflon-lined stainless-steel autoclaves. The solid products were centrifuged, washed with distilled water three times, and dried at 80 °C overnight. The dried solid was calcined at 550 °C for 6 hours to remove the organic template TPAOH. The samples synthesized with DMF, DMA, and DMP were named as TS-1-DMF, TS-1-DMA, and TS-1-DMP, respectively.

Synthesis of the control TS-1-C sample.

Control TS-1 zeolite (named as TS-1-C) was synthesized with the same molar

composition of the TS-1-CGM samples without adding any CGMs.

TPAOH (aq) treated TS-1-DMA zeolite

0.13 g TS-1-DMA sample was treated with 10 mL 0.19 M TPAOH aqueous solution for 12 hours at 170 °C under the rotation condition.

Syntheses of ZSM-5-C, ZSM-5-DMF and ZSM-5-DMA samples.

ZSM-5 samples were synthesized by hydrothermal method. The molar composition of the synthesis gels was SiO₂: 0.005Al₂O₃: 0.28 TPAOH: 0.19 NaOH: 34 H₂O: 0.37 CGM (CGM represents DMF or DMA). In a typical procedure, the TPAOH solution was added to water with continuous stirring. Then, NaOH and Al(OH)₃ were added into the solution. After several hours, TEOS were added dropwise to above solution under stirring. After TEOS were completely hydrolysis, CGM was added to the solution and the reaction mixture was stirred for another few hours. The reaction gel was crystallized at 170 °C for 24 hours under static conditions in Teflon-lined stainless-steel autoclaves. The obtained solid products were centrifuged, washed with distilled water for three times and dried at 80 °C overnight. The obtained solid was calcined at 550 °C for 6 hours to completely remove organic template TPAOH. The samples synthesized with DMF or DMA were named ZSM-5-DMF and ZSM-5-DMA respectively. The sample without any CGMs was named ZSM-5-C.

Catalytic reactions

Oxidative desulfurization of dibenzothiophene (DBT)

A certain amount of DBT was dissolved in n-octane to prepare the model fuel with the concentration of sulfur is about 500 ppm. The ODS reactivity was tested in a 25 mL two-neck glass flask equipped with a reflux condenser. In a typical run, the reaction was carried out with 10 mL model fuel, 0.05 g of zeolite catalyst, 0.028 g of n-octadecane and 0.056 g of TBHP at 333 K for 40 min. Afterwards, GC-MS (Thermo Fisher Trace ISQ, equipped with a TG-5MS column, 60 m 320 μm 25 μm) was utilized to analyze the reactant and products.

Epoxidation of 1-hexene.

Epoxidation of 1-hexene with H₂O₂ as oxidant was carried out in a 25 mL round-bottom flask equipped with a reflux condenser. In a typical operation, 0.05 g of catalyst, 10 mL of methanol, 10 mmol of 1-hexene and 10 mmol H₂O₂ (30 wt%) were added into a double-necked round bottom flask in sequence, and the reaction was carried out under continual magnetic stirring at 333 K for 120 min. Upon completion of the reaction, the liquid product was centrifuged and analyzed by GC-MS (Thermo Fisher Trace ISQ, equipped with a TG-5MS column, 60 m 320 μm 25 μm) and n-dodecane as internal standard. The conversion of 1-hexene and the selectivity of corresponding epoxy compounds were calculated.

Characterizations

The crystallinity and phase purity of the samples were determined by powder X-ray diffraction (PXRD) on Empyrean diffractometer (malvernpanalytical) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 KV), Rigaku MiniFlex600-C (40 KV, $\lambda = 1.5406 \text{ \AA}$) and Bruker D8 ADVANCE. Nitrogen adsorption/desorption measurements were carried out on a Micromeritics ASAP 3-flex analyzer at 77 K after degassing the samples at 350 °C under vacuum. Chemical compositions were determined by Inductively Coupled Plasma (ICP) analysis using an iCAP 7000 SERIES. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 X-ray photoelectron spectrometer using Al as the excitation source. Scanning electron microscopy (SEM) experiments were performed with JEOL JSM-6700F and JEOL JSM-7800F. Transmission electron microscopy (TEM) images were recorded on Talos F200s. Ti species were investigated by UV-vis diffuse reflectance spectroscopy (UV-Vis) over a range of 200 to 600 nm using a HITACHI U-4100. The baseline correction was carried out with powder BaSO₄. Fourier transform infrared (FT-IR) spectra were recorded on a BRUKER vertex 80v, samples were pelleted with KBr powder before testing. Thermal gravimetric (TG) analyses were performed using NETZSCH STA449F3 QMS403D and Bruker V70 at temperatures ranging from room temperature to 800 °C

at a heating rate of 10 °C min⁻¹. Ultraviolet Raman resonance spectroscopy (UV-Raman) were recorded on HS325 with exciting lines of 325 nm (the grating is 1200 gr/mm) and 266 nm (the grating is 2400 gr/mm). CHN analysis was executed on a PerkinElmer 2400 elemental analyzer.

Molecular electrostatic potential analysis

The Gaussian 09 and Gaussian View 5 packages were employed to conduct the molecular electrostatic potential (ESP) analysis of the title compounds. Minima and maxima of the ESP were generated in the Multiwfn software package and mapped onto the vdW surface.¹

Supplementary Figures

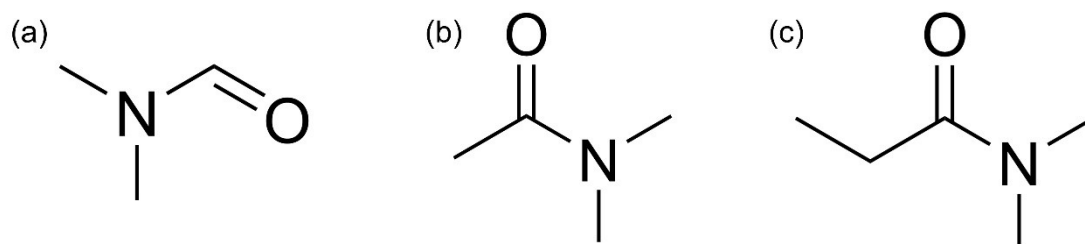


Fig. S1 Structures of (a) DMF, (b) DMA and (c) DMP.

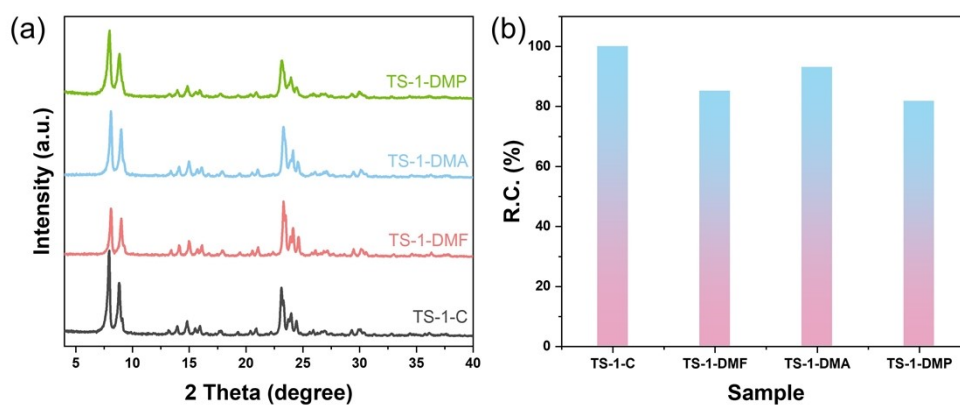


Fig. S2 (a) PXR D patterns and (b) relative crystallinity of synthesized samples.

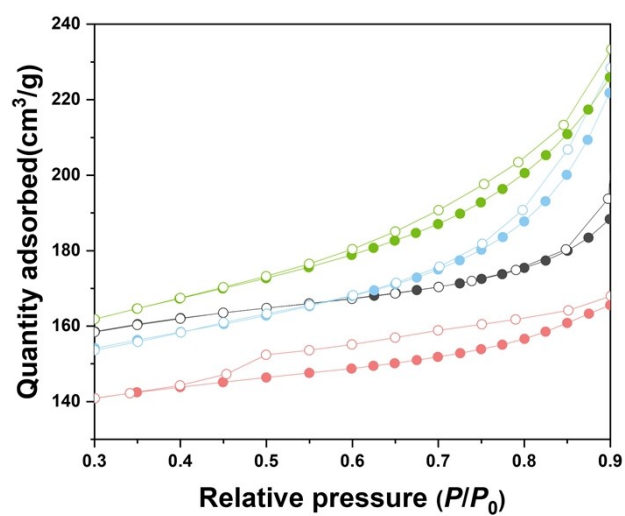


Fig. S3 N₂ adsorption–desorption isotherms in the regions of 0.3-0.9 P/P_0 of TS-1-CGMs samples (blank line: TS-1-C, red line: TS-1-DMF, blue line: TS-1-DMA, green line: TS-1-DMP).

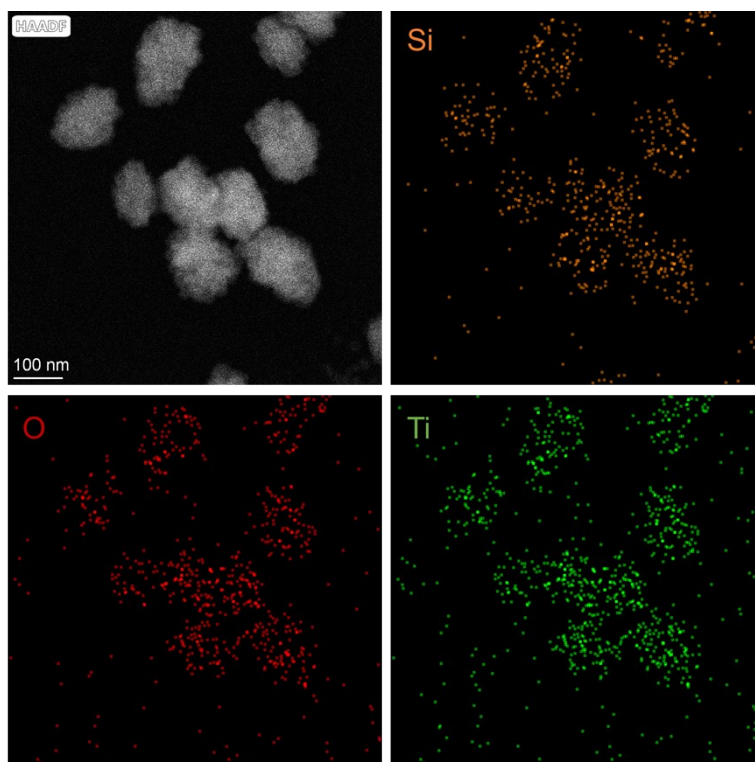


Fig. S4 HAADF STEM image and elemental mappings for O, Si and Ti elements of TS-1-DMA.

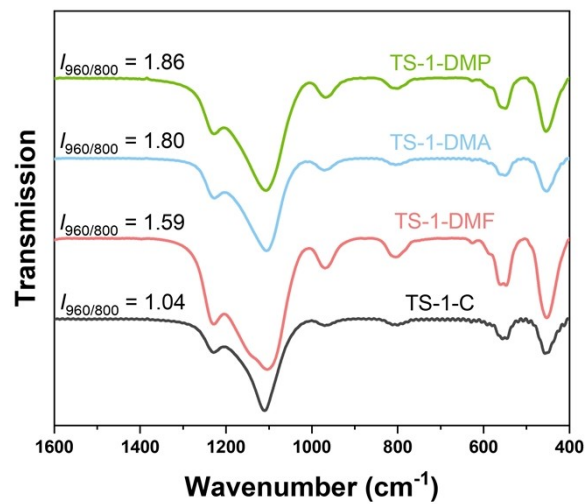


Fig. S5 FT-IR spectra of synthesized samples.

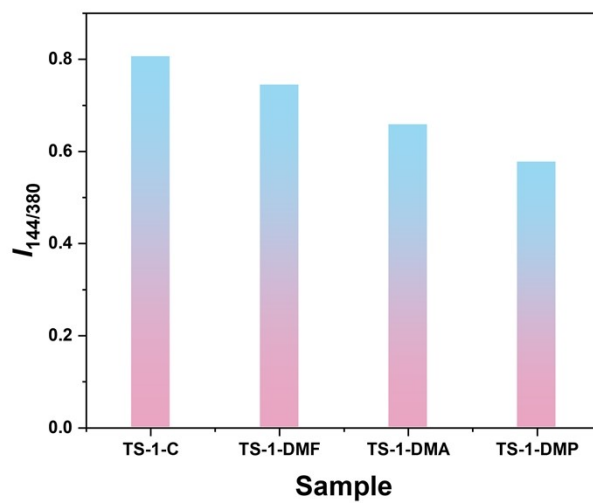


Fig. S6 $I_{144/380}$ calculated from UV-Raman spectra of samples.

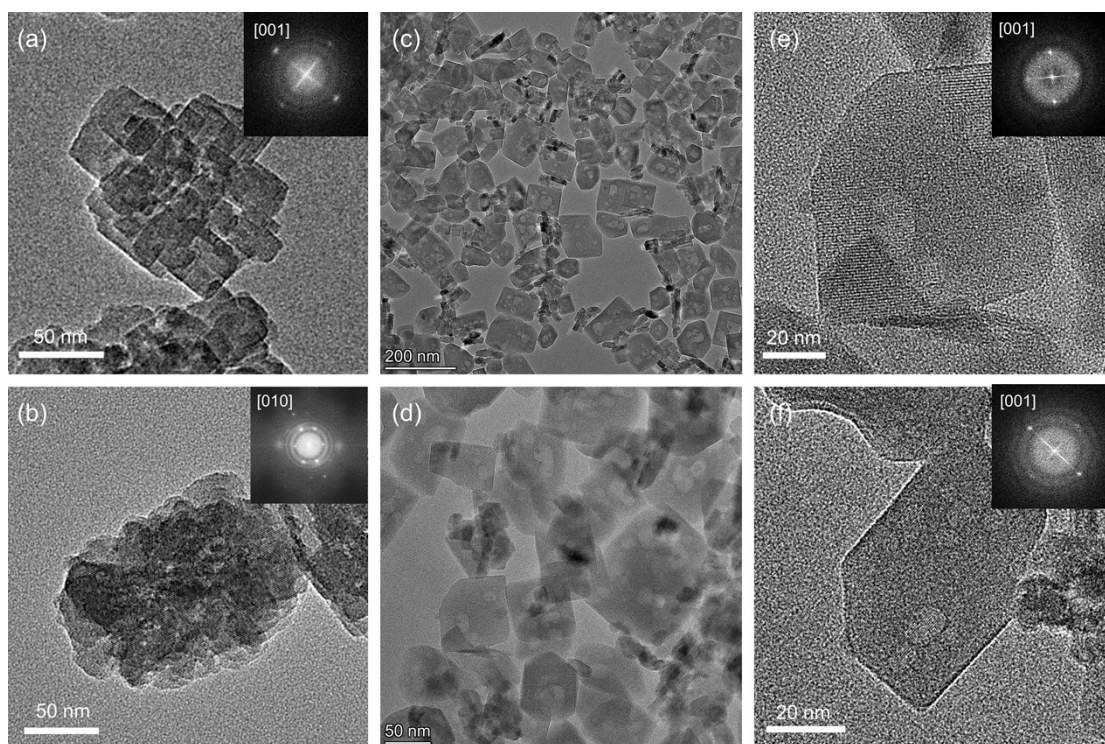


Fig. S7 TEM images of TS-1-DMA samples along the (a) [001] direction and (b) [010] direction. Low magnification TEM images (c, d) and high magnification TEM images (e, f) of TS-1-DMA treated with TPAOH aqueous solution. Inset: the corresponding FFT diffractograms.

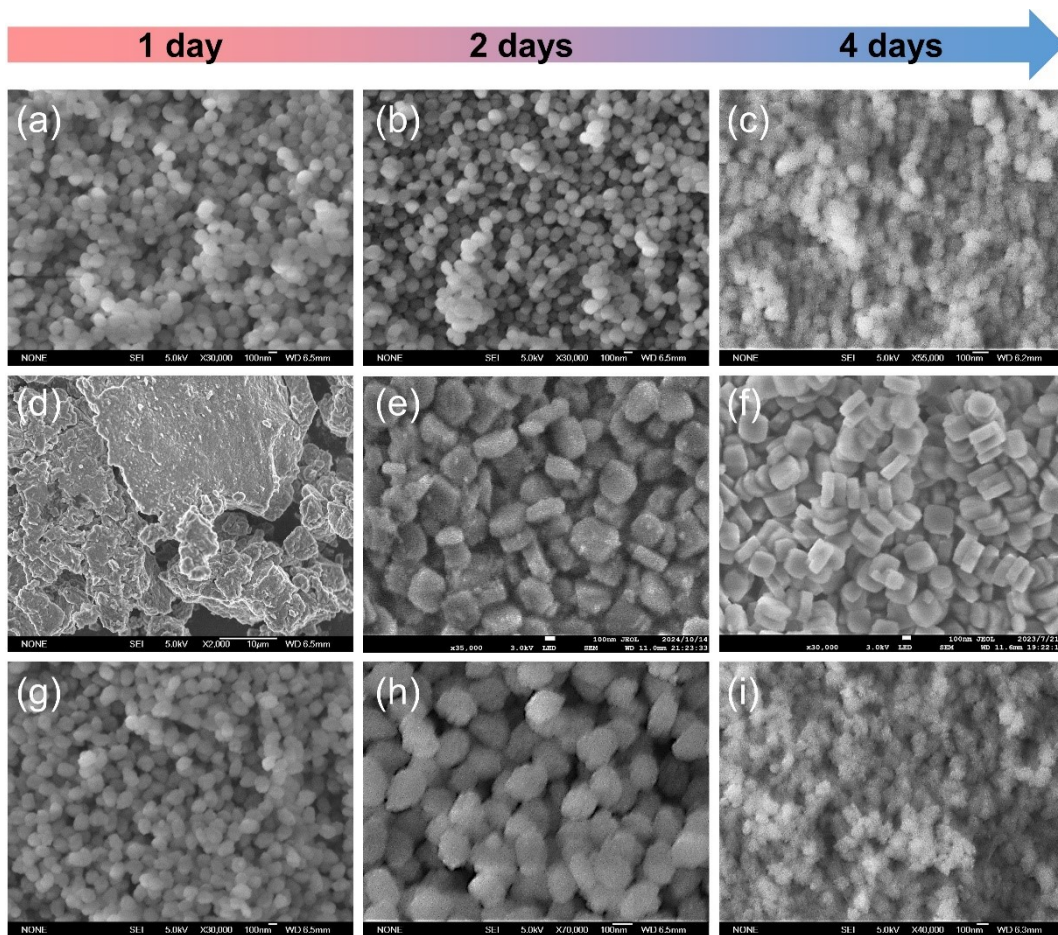


Fig. S8 SEM images of (a-c) TS-1-C, (d-f) TS-1-DMF and (g-i) TS-1-DMA samples crystallized at 120 °C for different time.

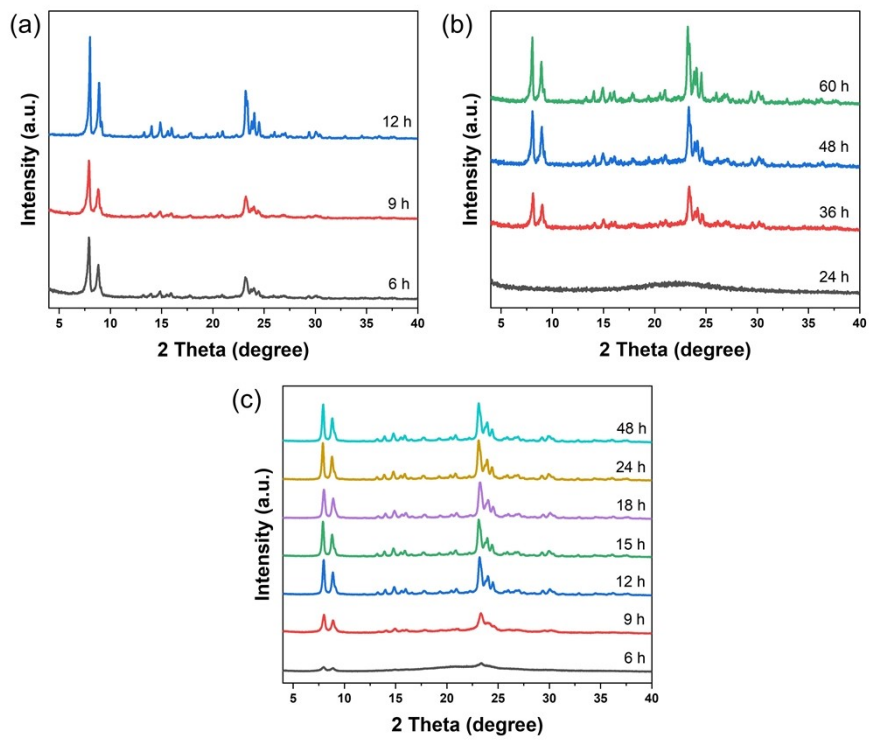


Fig. S9 PXR D patterns of (a) TS-1-C, (b) TS-1-DMF and (c) TS-1-DMA samples crystallized at 120°C for different time.

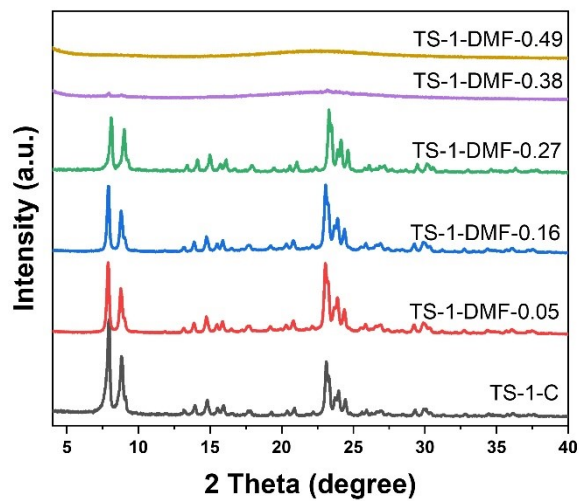


Fig. S10 PXR D patterns of synthesized samples with different $n(\text{DMF})/n(\text{SiO}_2)$.

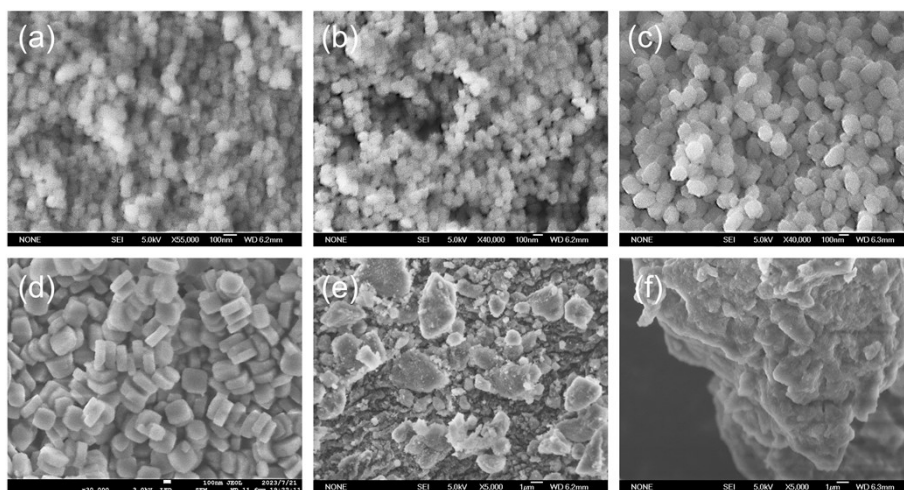


Fig. S11 SEM images of TS-1-DMF synthesized with varying $n(\text{DMF})/n(\text{SiO}_2)$ of (a) 0, (b) 0.05, (c) 0.16, (d) 0.27, (e) 0.38 and (f) 0.49 after crystallization at 120°C for 4 days.

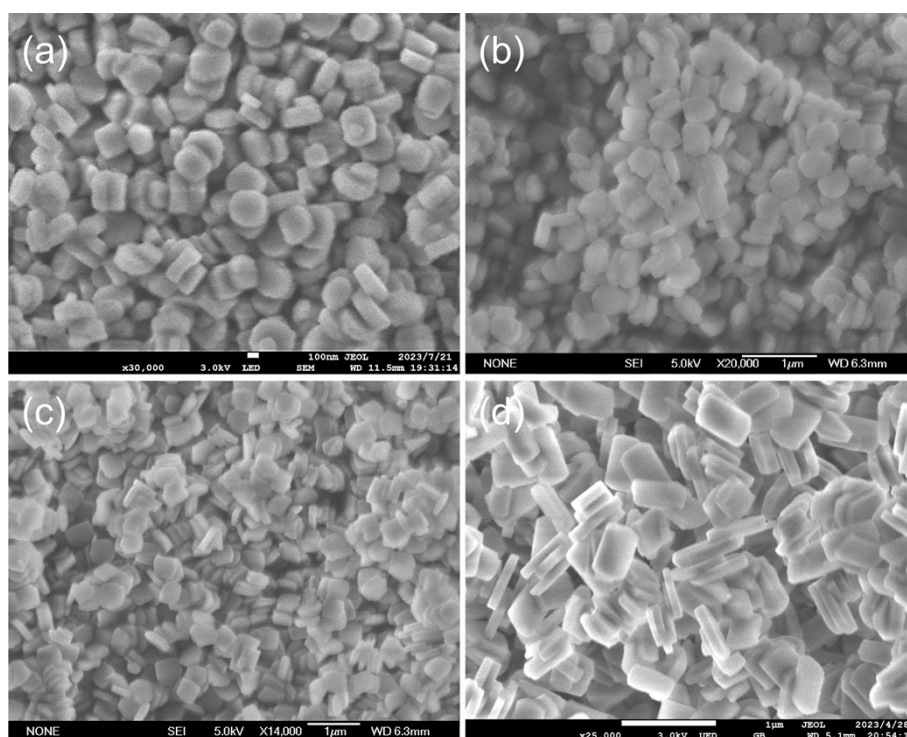


Fig. S12 SEM images of TS-1-DMF crystallized at (a) 80 °C for 24 hours and then at 120 °C for 4 days, (b) 80 °C for 3 hours and then at 140 °C for 4 days, (c) 80 °C for 3 hours and then at 170 °C for 4 days, (d) 170 °C for 4 days.

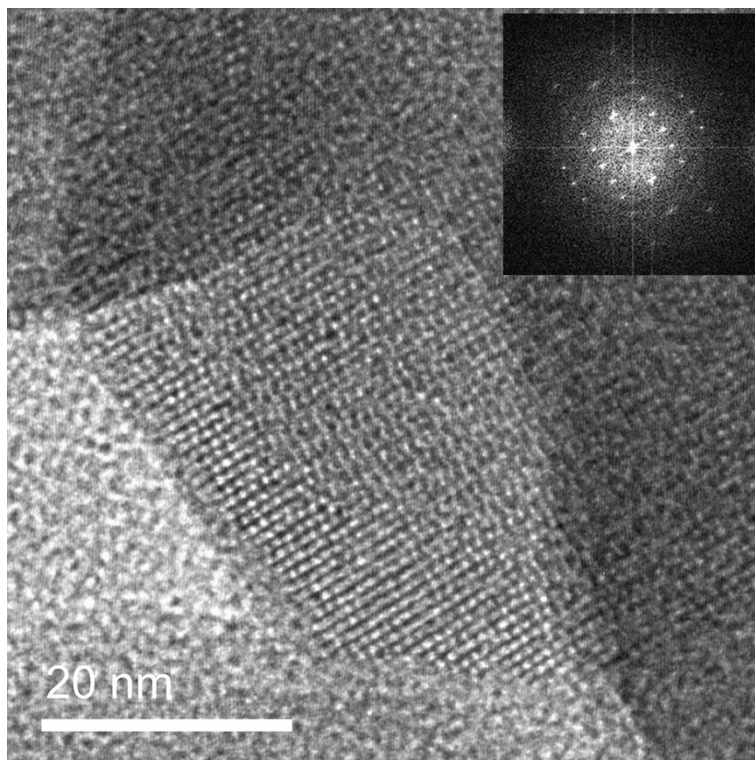


Fig. S13 TEM image of TS-1-DMA crystallized at 120 °C for 9 h. Inset: the corresponding FFT diffractogram.

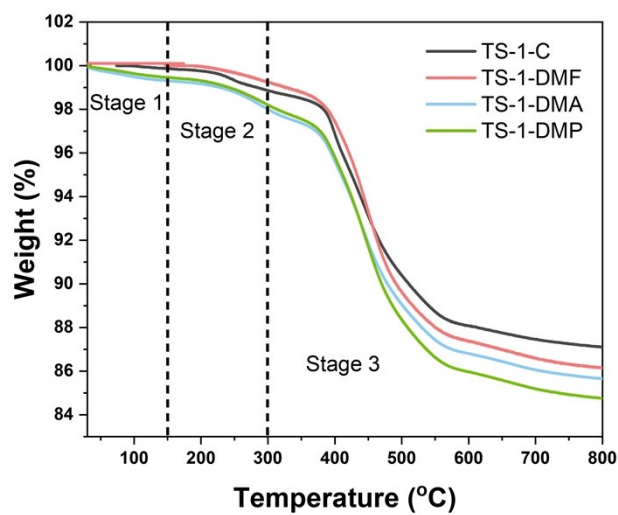


Fig. S14 TG curves of as-synthesized TS-1 samples.

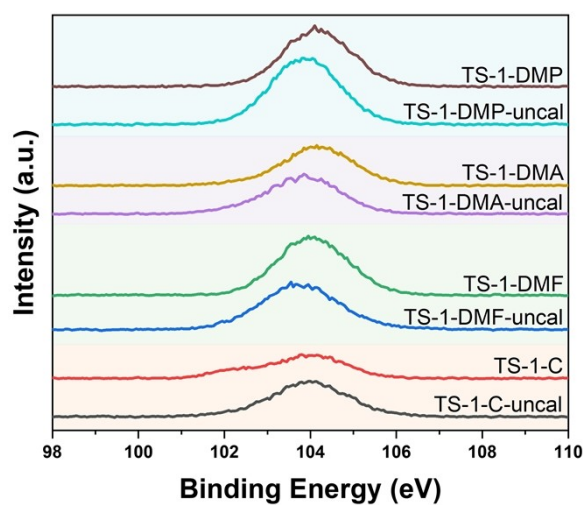


Fig. S15 XPS spectra of Si 2p of samples before and after calcination.

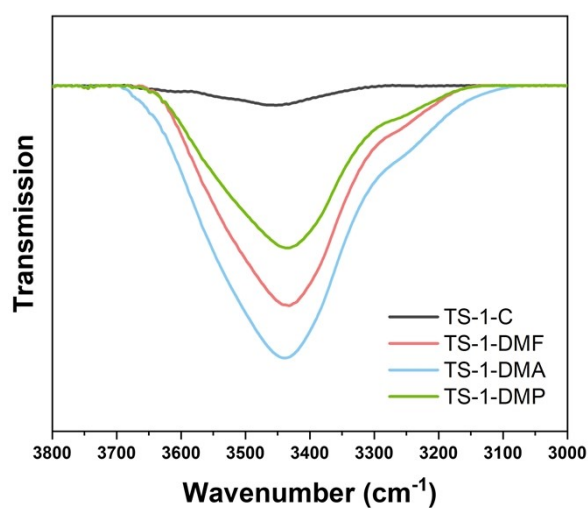


Fig. S16 The FT-IR spectra of synthesized samples after 300°C treatments.

Note: The TG curves of the samples show that the adsorbed water is eliminated after calcination at about 150°C. Here, we treated these samples at 300°C for 3 hours and immediately carried out FT-IR test to remove the interference of adsorbed water.

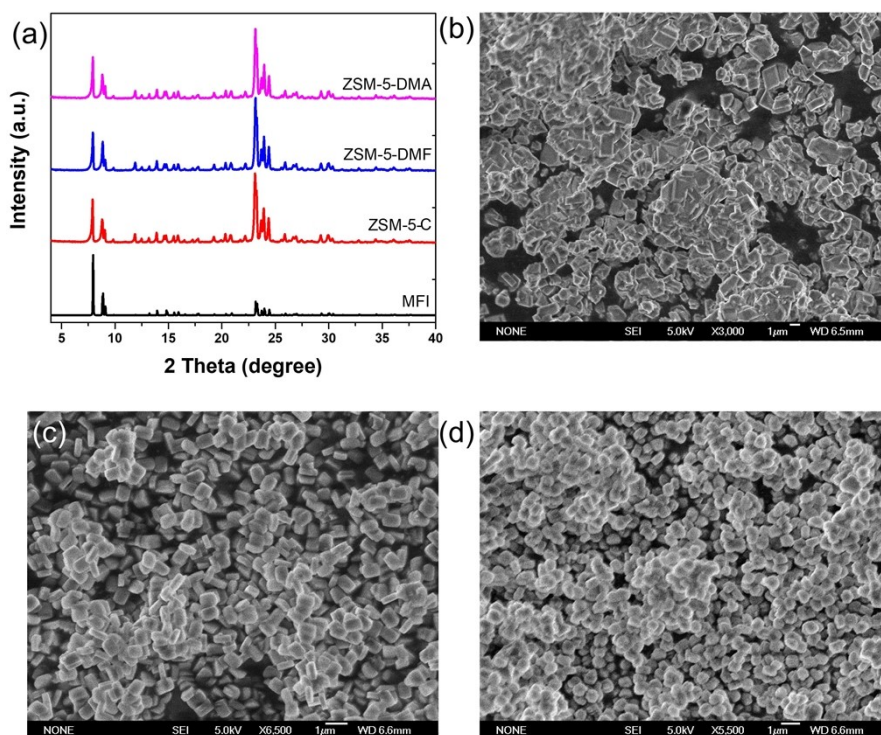


Fig. S17 (a) PXRD patterns of ZSM-5 samples. SEM images of ZSM-5 zeolite synthesized with (b) no CGMs, (c) DMF and (d) DMA.

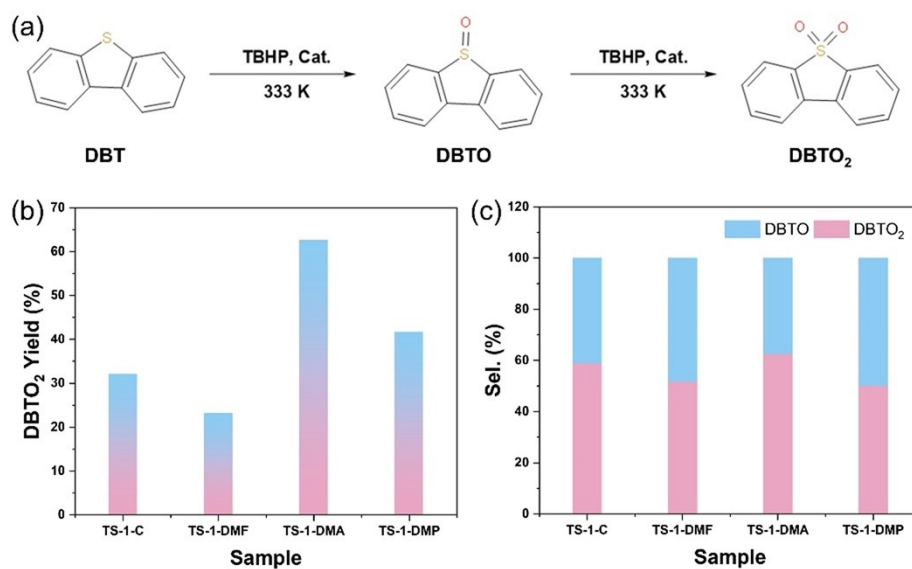


Fig. S18 (a) The reaction routes for the oxidative desulfurization of DBT. The DBTO₂ yield (b) and selectivity of DBTO and DBTO₂ (c) over synthesized samples.

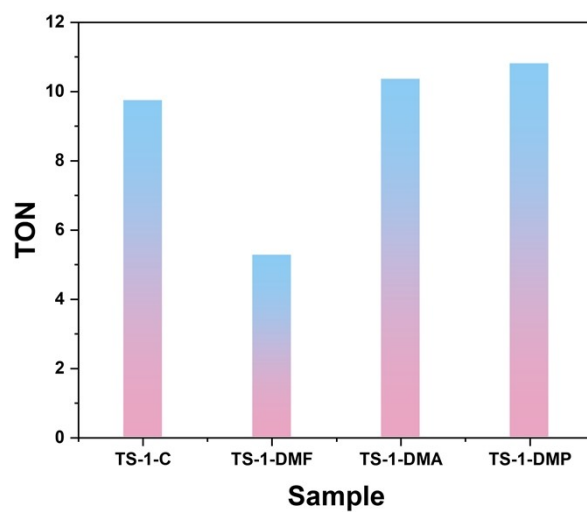


Fig. S19 TON of DBT (moles of converted DBT per mole of Ti site) over TS-1-CGMs samples.

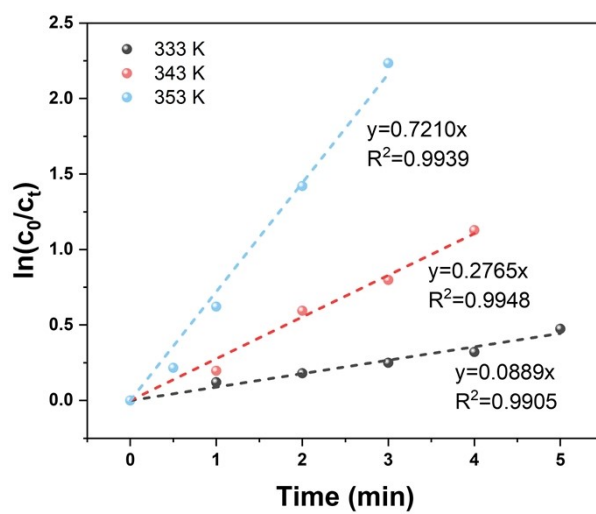


Fig. S20 Pseudo-first-order rate constants for the oxidation of DBT over TS-1-DMA at different temperatures.

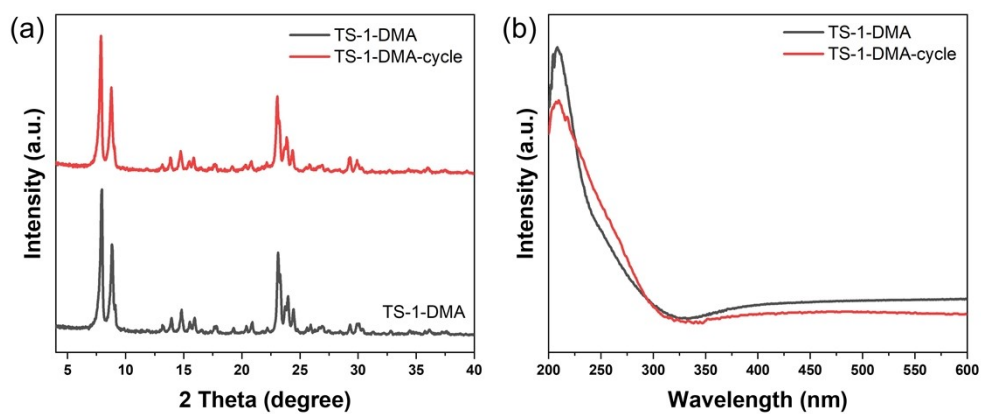


Fig. S21 (a) PXRD patterns and (b) UV-vis spectra of TS-1-DMA and TS-1-DMA after seven cycles.

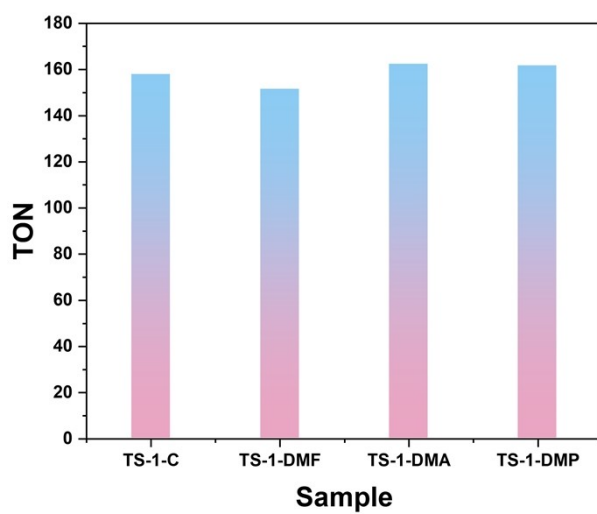


Fig. S22 TON of 1-hexene (moles of converted 1-hexene per mole of Ti site) over TS-1-CGMs samples.

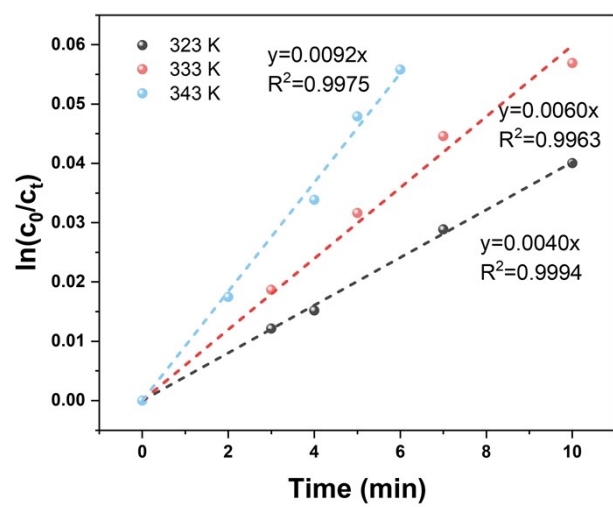


Fig. S23 Pseudo-first-order rate constants for the epoxidation of 1-hexene over TS-1-DMF at different temperatures.

Supplementary Tables

Table S1. Textural properties and Si/Ti ration of various TS-1 samples.

	S_{BET} (m^2g^{-1}) ^a	S_{micro} (m^2g^{-1}) ^b	S_{ext} (m^2g^{-1}) ^b	V_{total} (cm^3g^{-1}) ^c	V_{micro} (cm^3g^{-1}) ^d	V_{meso} (cm^3g^{-1}) ^e	Si/Ti ^f
TS-1-C	554	349	205	0.52	0.14	0.38	97.0
TS-1-DMF	506	335	171	0.29	0.14	0.15	63.4
TS-1-DMA	559	341	218	0.74	0.14	0.60	55.4
TS-1-DMP	565	337	228	0.66	0.14	0.52	66.0

^aSurface area was calculated from the nitrogen adsorption isotherm using the BET method.

^b S_{micro} (micropore area), S_{ext} (external surface area) were calculated using the t-plot method.

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

^d V_{micro} (micropore volume) was calculated using the t-plot method.

^e V_{meso} (mesopore volume) = $V_{\text{total}} - V_{\text{micro}}$.

^fDetermined by ICP.

Table S2. Compositional analyses of the as-synthesized samples.^a

	C (wt.%)	H (wt.%)	N (wt.%)	C/N
TS-1-C	10.07	1.961	0.89	11.31
TS-1-DMF	10.14	2.022	1.01	10.04
TS-1-DMA	9.99	2.047	1.21	8.26
TS-1-DMP	10.17	2.045	0.99	10.27
TPAOH (Cala.)	-	-	-	10.28
DMF (Cala.)	-	-	-	2.57
DMA (Cala.)	-	-	-	3.43
DMP (Cala.)	-	-	-	4.29

^a Elemental analysis was based on a CHN elemental analyses.

Table S3. The catalytic activities for the epoxidation of 1-hexene over different TS-1 samples.

Sample	Si/Ti	Con. (%)	Sel. (%)	References
TS-1-DMF	63.4	19.5	97.9	This work
TS-1#0.15-12h-0.2ly	58	22.7	>95	2
TS-1#0.15-12 h-F	108	<10	97	2
TS-1-50-healed	50	44	79	3
TS-1-urea-seed a-pre	-	50.6	58.6	4
MTS-PTS	49	30.6±0.4	96.2±0.4	5
MTS-HU ₂	50	34.8±0.4	98.4±0.4	5
HTS-1#S0.25	39.63	24	96	6
TS-1-TL0.2-36 ^a	36.9	33.9	95.0	7
TS-1#B_15Et:0.6LC	38.3	55	96	8
TS-1-AM	80	28	90	9

Notes and references

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