Supplementary Information

Dual-additive engineering of Ti sites and mesoporosity in TS-1 zeolite for enhanced oxidative desulfurization

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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), acetonitrile (98%, Macklin), (3-cyanopropyl)-triethoxysilane (98%, Adamas), dibenzothiophene (DBT, 98%, Macklin), tert-butyl hydroperoxide solution (70 wt%, Macklin).

Preparation of TS-1 zeolites

The TS-1 zeolites were synthesized with the following molar composition: 1 SiO₂: 0.0256 TiO₂: 0.4 OSDA: 15 H₂O: 0-0.1 Additive. Tetrapropylammonium hydroxide (TPAOH) was used as the organic structure-directing agent, and tetrabutyl titanate (TBOT) served as the titanium source. The typical synthesis procedure is as follows: TPAOH (40 wt%) is mixed with distilled water, followed by the addition of TBOT and stirring for 1 hour. Next, tetraethyl orthosilicate (TEOS) and additives are introduced into the mixture, and stirring is continued for 12 hours to complete hydrolysis. The resulting gel is then transferred into a Teflon-lined stainless-steel autoclave for crystallization. The precursor mixture underwent an aging step at 80 °C for 24 h, followed by static hydrothermal crystallization at 170 °C for 24 h. After crystallization, the products are separated by centrifugation, washed sequentially with water and ethanol, then dried and calcined at 550 °C for 8 hours in 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 α radiation (λ = 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.

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) was 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.

Ultraviolet Raman resonance spectroscopy (UV-Raman)

The Ultraviolet Raman resonance spectroscopy (UV-Raman) was recorded on a HS325 Raman spectrometer using the 325 nm line laser and 266 nm line laser as the excitation source and with a Princeton CCD as the detector.

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

The ¹H and ²⁹Si 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 ¹H MAS NMR experiments were performed using a $\pi/2$ ¹H pulse length of 4.0 µs, a repetition time of 2 s, and 32 scans. For the two-dimensional (2D) ¹H-¹H double quantum (DQ) single quantum (SQ) MAS NMR measurements, DQ coherences were excited and reconverted with a POST-C7 pulse sequence.¹ The increment interval in the indirect dimensional data sets consisted of 128 t₁ × 256 t₂. The ¹H MAS NMR signals were referenced to adamantane (1.82 ppm).

²⁹Si MAS NMR spectra with high power proton decoupling was recorded on a 4.0 mm probe, using a $\pi/2$ pulse of 5.1 µs, a recycle delay of 80 s and 128 scans.

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 being 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 out at 343 K for 30 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 × 320 μ m × 0.1 μ 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%.

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

$$k = A e^{-Ea/RT}$$

Where: *k* is the observed rate constant; *A* is the pre-exponential factor; *E*a is the activation energy (J mol⁻¹); *R* is the universal gas constant (8.314 J mol⁻¹K⁻¹); and *T* is the temperature (K).

Supplementary figures and tables



Figure S1. PXRD patterns of synthesized samples.



Figure S2. STEM image of TS-1-NA.



Figure S3. STEM image of TS-1-CN.



Figure S4. STEM image of TS-1-CNS.



Figure S5. STEM image of TS-1-DA.



Figure S6. (a-b) SEM images of TS-1-NA.



Figure S7. (a-b) SEM images of TS-1-CN.



Figure S8. (a-b) SEM images of TS-1-CNS.



Figure S9. (a-b) SEM images of TS-1-DA.



Figure S10. HAADF-STEM image and EDS elemental mappings of TS-1-NA.



Figure S11. HAADF-STEM image and EDS elemental mappings of TS-1-CN.



Figure S12. HAADF-STEM image and EDS elemental mappings of TS-1-CNS.



Figure S13. PXRD patterns of different crystallization times of (a) TS-1-NA and (b) TS-1-DA.



Figure S14. Photos of initial synthetic mixtures with different crystallization time of TS-1-DA and TS-1-NA.



Figure S15. FT-IR spectra of synthesized samples.



Figure S16. Pore size distributions of synthesized samples.



Figure S17. ²⁹Si MAS NMR spectra of synthesized samples.



Figure S18. UV-vis spectra of TS-1 synthesized through the dual-additive synthesis strategy.



Figure S19. Raman spectra under excitation at 325 nm of different crystallization times of (a) TS-1-NA and (b) TS-1-DA.



Figure S20. Raman spectra under excitation at 266 nm of different crystallization times of TS-1-DA.



Figure S21. PXRD patterns of different crystallization times of TS-1-DA.



Figure S22. XPS spectra of Ti 2p_{3/2} of (a) TS-1-NA, (b) TS-1-CN, (c) TS-1-CNS and (d) TS-1-DA before and after calcination.

Note: In the samples with additives, the strong interaction between the cyano-functional group and the titanium species increases the electron density around titanium, causing the Ti 2p signal peak to shift to lower electron energies. After calcination, acetonitrile is replaced by water molecules, and hexa-coordinate titanium species are formed in the TS-1-CN and TS-1-DA samples, with peak center shifts from 458.8 eV to 460.1 eV and from 457.6 eV to 460.3 eV, respectively. Furthermore, after calcination, cyano-silane promotes the interaction between silicon and titanium, leading to more titanium species incorporated into the framework and increase the TiO₄ content in the TS-1-CNS and TS-1-DA samples. The TS-1-DA exhibits lower electron energy compared to other samples before calcination (457.6eV), and a greater energy shift after calcination (2.7eV), indicating that the additives exhibit stronger interaction with Ti species and more titanium species may interact with the cyano-functional group, thus leading to a higher Ti content in the sample (including tetra-coordinated framework Ti species and the hexa-coordinated Ti species).



Figure S23. TG curves of synthesized samples.



Figure S24. The correlation between $ln(c_0/c_t)$ and reaction time over TS-1-DA. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg of TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 2 min.

Note: A good correlation between ln(c0/ct) and reaction time over TS-1-DA indicates a first-order dependence of DBT conversion on reactant concentration.



Figure S25. (a) Time-course variation of DBT conversion with various Ti concentrations. Reaction conditions: 10 mL of 500 ppm model fuels, TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 30 min. (b) Time-course variation of DBT conversion with various DBT concentrations. Reaction conditions: 10 mL model fuels, 30 mg TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 75 min. (c) Time-course variation of DBT conversion with various Ti concentrations. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 75 min. (c) Time-course variation of DBT conversion with various Ti concentrations. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg TS-1-DA catalyst, 343 K, 30 min.



Figure S26. (a) The pseudo first-order rate constant for different concentrations of the TS-1-DA catalyst at 343 K; (b) The pseudo first-order rate constant for different concentrations of DBT at 343 K; (c) pseudo zero-order rate constant for different concentrations of TBHP.

Note: The DBT reaction rate exhibits first-order dependence on both Ti content (catalyst loading) and DBT concentration. In contrast, TBHP concentration shows negligible influence on the rate, consistent with a zero-order dependence.



Figure S27. PXRD patterns of fresh TS-1-DA and used TS-1-DA after 5 cycles of DBT oxidation.



Figure S28. UV-vis spectra of fresh TS-1-DA and used TS-1-DA after 5 cycles of DBT oxidation.



Figure S29. (a-b) TEM images of used TS-1-DA after 5 cycles of DBT oxidation.



Figure S30. PXRD patterns of fresh TS-1-DA and used TS-1-DA after 10 cycles of DBT oxidation.



Figure S31. UV-vis spectra of fresh TS-1-DA and used TS-1-DA after 10 cycles of DBT oxidation before and after calcination.



Figure S32. (a) Time-dependent conversion of DBT. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 30 min. (b)PXRD pattern and (c) UV-vis spectra of TS-1-DA after HNO₃ treatment.

Note: To verify the catalytic activity of hexa-coordinated Ti species, we treated TS-1-DA with HNO_3 at 100 °C for 6 hours to remove a portion of the hexa-coordinated titanium species. UV-vis spectroscopy and ICP measurements revealed a decrease in the hexa-coordinated titanium species in TS-1. In the desulfurization of DBT, the desulfurization performance of the nitric acid-treated sample showed a significant decline, thereby confirming the catalytic activity of the hexa-coordinated titanium species.



Figure S33. Time-dependent conversion of Th and DBT. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 30 min. Note: While the hierarchical structure of TS-1-DA eliminates steric and mass transfer limitations (as confirmed by pore-size distribution and diffusion studies), the conversion of thiophene reached only ~50% after 30 min, significantly lower than the near-complete DBT conversion observed in our earlier tests. This difference in activity can be attributed to the inherent electronic properties, the nucleophilic characteristic, of the sulfur-containing compounds. DBT's sulfur atom exhibits higher nucleophilicity due to its extended aromatic system, which delocalizes electron density onto the sulfur atom, making it more susceptible to oxidation. In contrast, thiophene's compact five-membered ring limits electron donation to the sulfur atom, resulting in weaker nucleophilic character and higher resistance to oxidative attack.



Figure S34. Time-dependent conversion of DBT in different solvents. Reaction conditions: 10 mL of 500 ppm model fuels, 30 mg TS-1-DA catalyst, n(sulphide)/n(TBHP) was 0.5, 343 K, 30 min. Note: It can be observed that TS-1-DA exhibits excellent desulfurization efficiency in n-hexane and n-octane, while the desulfurization rate decreases in n-dodecane, which has a higher carbon number. The increase in reaction rate with decreasing carbon number of the solvent can be attributed not only to the larger diffusion coefficient of DBT but also to its improved wettability with the interfacial phase. Both factors enhance the mass transfer of DBT, thereby promoting its oxidation rate. In polar solvents, the reaction rate significantly decreases, which is due to the interaction between the TBHP oxidant and the hydrophobic TS-1 zeolite being hindered in polar solvents.



Figure S35. (a) Photos, (b)PXRD patterns and (c) UV-vis spectra of TS-1-DA synthesized under different scales.

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Sample	SBET	Smicro	Sext	V _{total}	Vmicro	V _{meso}	Si/Ti ^f	Si/Ti ^g	I960/800 ^h
	$(m^2/g)^a$	$(m^{2}/g)^{b}$	$(m^2/g)^b$	(cm ³ /g) ^c	(cm ³ /g) ^d	(cm ³ /g) ^e			
TS-1-NA	435	367	68	0.44	0.15	0.29	40.6	36.0	1.43
TS-1-CN	492	353	139	0.86	0.14	0.72	33.2	20.4	1.49
TS-1-CNS	506	402	104	0.46	0.16	0.30	29.7	31.5	1.45
TS-1-DA	516	373	143	0.44	0.15	0.29	25.6	24.3	1.96

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

^a Surface 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_{total} (total pore volume) - V_{micro}.

^f Measured by inductively coupled plasma (ICP).

^g Measured by X-ray photoelectron spectroscopy (XPS).

^h Infrared spectra (IR) relative intensity of the bands at 960 and 800 cm⁻¹.

Sample	Mass of	Temp.	Reaction	Removal of	Rof	
	catalyst (mg)	(K)	time (min)	DBT (%)	ĸei.	
TS-1-DA	30	343	20	100	This work	
TS-1-DMA	50	333	20	100	Ref.S2	
TS-1-DMP	50	333	20	89.7	Ref.S2	
TS-1-C	50	333	20	54.3	Ref.S2	
TS-1-DMF	50	333	40	52.8	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	
0.030PTS	150	333	45	98.5	Ref.S4	
CTS	150	333	45	21.5	Ref.S4	
0.180PTS	150	333	45	58.2	Ref.S4	
0.090PTS	150	333	45	60.7	Ref.S4	
0.015PTS	150	333	45	85.6	Ref.S4	
0.010PTS	150	333	45	29.5	Ref.S4	
TS-1(H1)	55	333	15	100	Ref.S5	
TS-1(H3)	55	333	15	100	Ref.S5	
TS-1(C3)	55	333	15	60.7	Ref.S5	
TS-1A	50	333	15	68.1	Ref.S6	
TS-1B	50	333	15	70.0	Ref.S6	
TS-1C	50	333	15	73.1	Ref.S6	
TS-1-h	50	333	360	62.0	Ref.S7	
TS-1-d	50	333	360	99.0	Ref.S7	
HTS-1-50	50	333	30	100	Ref.S8	
TS-1-50-CP	50	333	30	94	Ref.S8	

 Table S2. Comparison of catalytic performance over synthesized samples and some representative

 TS-1 catalysts in oxidation desulfurization of DBT

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