Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

An amino acid-assisted approach to fabricate nanosized hierarchical TS-1 zeolites for efficient oxidative desulfurization

Guoju Yang[a,b], Ji Han[a], Ziyi Qiu[a], Xiaoxin Chen,*[a,c] Zhaochi Feng[d] and Jihong Yu* [a,b]

[a.] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

E-mail: **chenxiaoxin@jlu.edu.cn**, **jihong@jlu.edu.cn**

[b.] International Center of Future Science, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

[c.] Electron Microscopy Center, Jilin University

[d.] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Table of Contents

1. **Experimental section**

   Chemicals and materials

   Synthesis of materials

   Characterizations

   Catalytic tests

2. **Supplementary Figures and Tables**

3. **References**

Experimental Section

Chemicals and materials

The reagents used in this work include tetraethylorthosilicate (TEOS) (Beijing Chemical Works), tetrabutyl orthotitanate (TBOT) (98%, Sinopharm), tetrapropylammonium hydroxide (TPAOH) (25%, Sinopharm), $_{\mathrm{L}}$-lysine ($C_6H_{14}N_2O_2$, Aladdin Biochemical Technology Co., 98%), tert-butyl hydroperoxide (TBHP) (65%, Sinopharm Chemical Reagent Co.). Ceric sulfate and 1-octane were purchased from Beijing Chemical Works. Dibenzothiophene (DBT) (98%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (99%) were purchased from Aladdin Biochemical Technology Co..

Synthesis of materials

Synthesis of nanosized hierarchical TS-1 and micron-sized microporous counterparts: The molar composition of the mixture was set to 1.0 SiO_2: 0.54 TPAOH : 0.015 TiO_2 : x $_{\mathrm{L}}$-lysine : 18 H_2O (x=0, 0.2, 0.4 and 0.6) under two-step rota-crystallization for the synthesis of nanosized hierarchical TS-1 and micron-sized microporous counterparts. Typically, TPAOH and TEOS were mixed at room temperature under stirring until TEOS was hydrolyzed completely, and then TBOT was added dropwise to a mixture of TPAOH and TEOS under vigorous stirring for 8 h, then followed by addition of a certain amount of $_{\mathrm{L}}$-lysine. The resulting solution was transferred into a Teflon-lined stainless steel autoclave and then crystallized in a homogeneous reactor initially at 80 °C for 2 days and further at 170 °C for 1 day under two-step rotational conditions with a rotation rate of 40 rpm. The as-synthesized solid products were centrifuged, washed with water and ethanol several times, and dried at 80 °C in an oven overnight, followed by calcination at 550 °C for 6 h. The calcined samples were denoted as TS-L_0R, TS-$L_{0.2}$R, TS-$L_{0.4}$R and TS-$L_{0.6}$R, respectively. As for TS-$L_{0.4}$S, it was synthesized under similar conditions to that of TS-$L_{0.4}$R but under static crystallization conditions by using a conventional oven.

Characterization

Powder X-ray diffraction analysis of the as-synthesized TS-1 samples were performed on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 50 KV). The scanning electron microscope (SEM) were measured on a JSM6700F electron microscope. Transmission electron microscopy (TEM) and STEM-energy-dispersive X-ray spectrometry (EDX) analysis were measured on JEM-2200FS and JEM-2100 microscope coupled with X-Max EDS-detector from Oxford Instruments, respectively. The textural properties of TS-1 materials were obtained via Nitrogen adsorption-desorption analysis with a Micromeritics ASAP 2020 Plus analyzer at 77 K. Chemical compositions of as-synthesized TS-1 samples were determined with Inductively Coupled plasma-optical emission spectrometry (ICP-OES) on an iCAP 7000 SERIES. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 X-ray photoelectron spectrometer using Al as the exciting source. The spectral resolution was 4 cm^{-1} and the laser power at the sample was less than 5 mW. Infrared spectra (IR) were recorded by Nicolet Impact 410 FT-IR Infrared Instrument using KBr pellet technique. The Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis) of the materials was recorded over the range of 200 nm to 500 nm against the support as reference on a SHIMADZU U-4100. 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.

Catalytic tests

The oxidation of dibenzothiophene (DBT) or 4,6-dimethylbenzothiophene (4,6-DMDBT):

A certain amount of sulphide (DBT or 4,6-DMDBT) was dissolved in n-octane as model fuel, and the concentration of sulfur in the model fuel is 500 ppm. The reaction was performed in a two-neck glass flask (25 mL) heating in an oil bath under vigorous stirring (600 rap/min). Specifically, 7 g of model fuel and 50 mg of catalyst were added to the flask in the oil bath. Then the tertbutylhydroperoxide (TBHP) as oxidant was charged in the flask, in which the molar ratio of TBHP/DBT was fixed to be 2. The reaction was performed at 60 °C for the required time. Then, the reacted solution was filtered and analyzed by gas chromatography (Agilent 7890B) equipped with HP-innowax column (30 m × 320 µm × 25 µm). In addition, the conversion of TBHP was obtained by titration with $Ce(SO_4)_2$ and ferroin indicator. The n-pentadecane was used as the internal standard, and mass balances are above 95%.

The recycling test was carried out as the following steps: the TS-$L_{0.4}$R catalyst after the first reaction run was centrifuged and washed with water for three times. Afterwards, the obtained sample was dried at 100 °C overnight, followed by calcination at 550 °C for 5 hours. Eventually, the regenerated sample was applied for the reaction by the aforementioned operation procedures. The sample recycling test was repeated five times in total.

The turnover number (TON) = n(sulphide)$_{initial}$ - n(sulphide)$_{residual}$ / n(Ti), where n(sulphide)$_{initial}$ and n(sulphide)$_{residual}$ represent the molar of initial and residual sulfur contents in the model oil, respectively.

Supplementary Figures and Tables

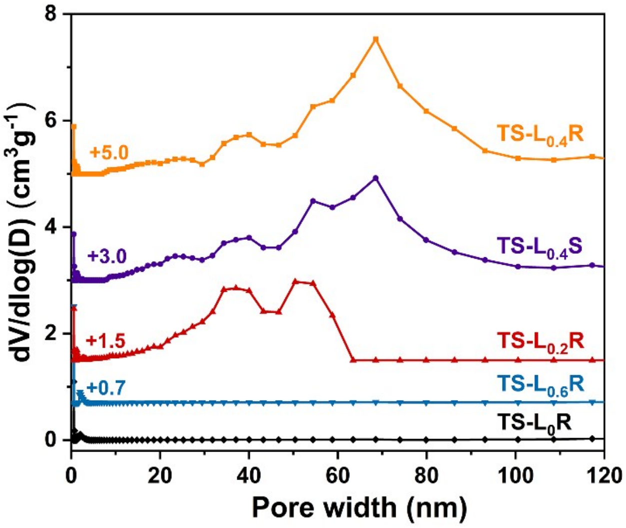

Fig. S1 Pore size distributions of microporous TS-1 (TS-L$_{0.6}$R and TS-L$_0$R) and nanosized hierarchical TS-1 (TS-L$_{0.2}$R, TS-L$_{0.4}$S and TS-L$_{0.4}$R).

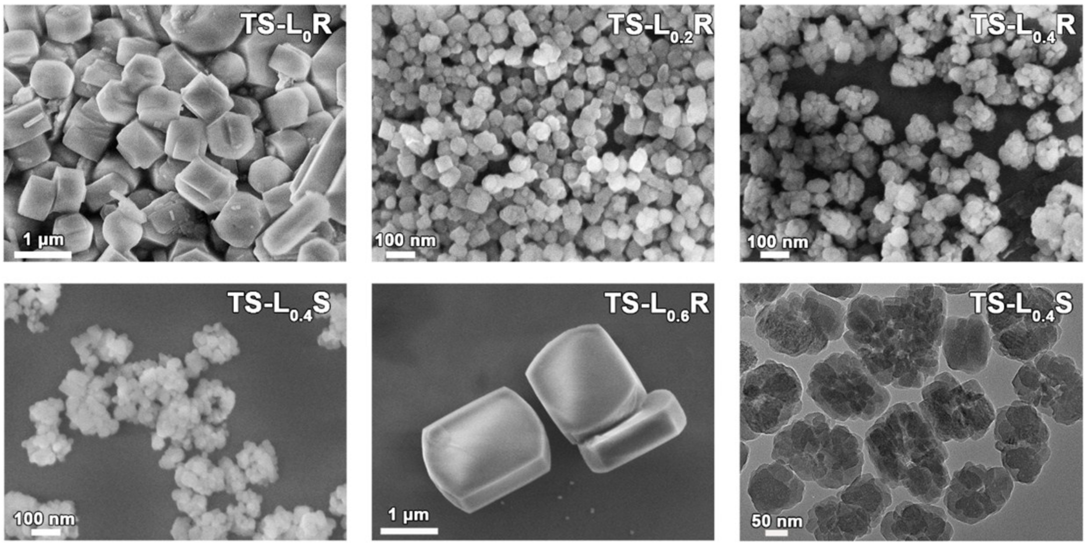

Fig. S2 SEM images of prepared TS-1 samples and TEM image for hierarchical TS-$L_{0.4}$S sample.

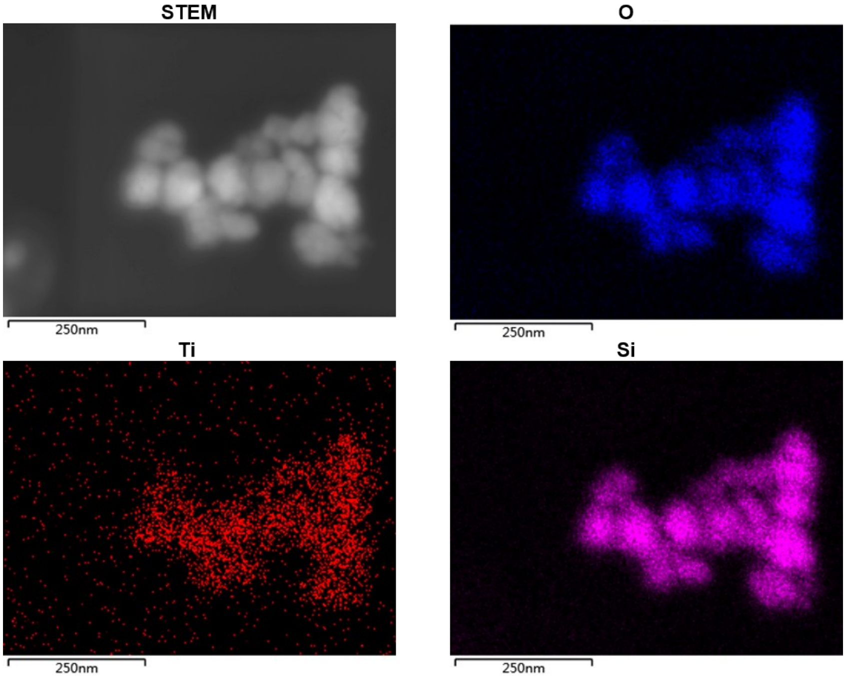

Fig. S3 The STEM-energy-dispersive X-ray spectrometry (EDX) analysis for the TS-$L_{0.4}$R sample.

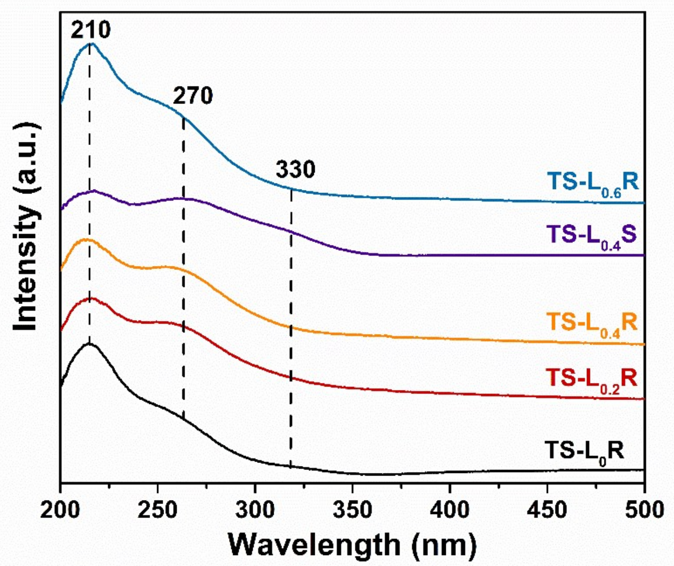

Fig. S4 UV-vis spectra of microporous TS-1 (TS-L_0R and TS-$L_{0.6}$R) and nanosized hierarchical TS-1 (TS-$L_{0.2}$R, TS-$L_{0.4}$S and TS-$L_{0.4}$R).

UV-visible spectroscopy is employed to investigate the Ti coordination states in all the samples. As shown in Fig. S4, the absorption band at around 210 can be observed in all the samples, which originates from the tetracoordinated titanium.[1] However, a weak absorption band at 330 nm only appears in TS-$L_{0.4}$S sample, suggesting the presence of some anatase TiO_2 species,[2] which is in accordance with more surface Ti content detected by XPS measurement. This indicates that the rota-crystallization is advantageous to avoid the formation of anatase TiO_2.[3]

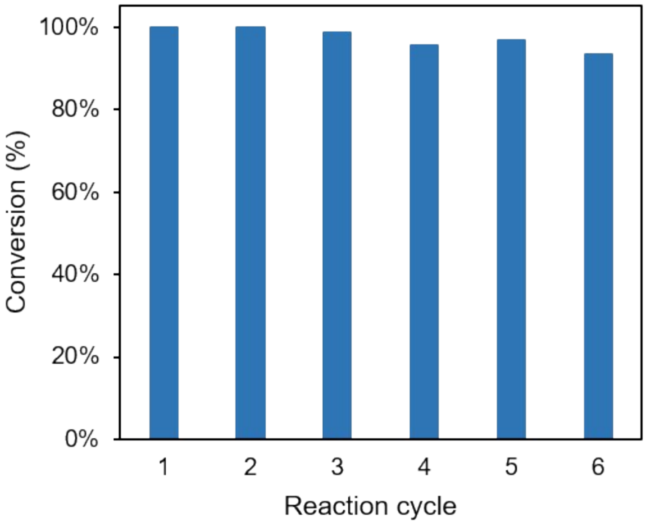

Fig. S5 Recycle tests in the oxidation of DBT over TS-$L_{0.4}$R material. Reaction condition: 10 mL

DBT model fuels (500 ppm of S), 50mg TS-L$_{0.4}$R, n(TBHP) / n(DBT) was 2, at 60 °C for 30 min.

Table S1 Oxidative desulfurization of DBT and 4,6-DMDBT over TS-1 samples[a]

		DBT oxidation			4,6-DMDBT oxidation		
Catalyst	Ti[b] (wt%)	Con.$_{\text{DBT}}$ (%)	Con.$_{\text{TBHP}}$ (%)	TON[c]	Con.$_{\text{4,6-DMDBT}}$(%)	Con.$_{\text{TBHP}}$ (%)	TON[c]
TS-L$_0$R	0.76	37.5	32.8	5.2	12.6	13.8	1.8
TS-L$_{0.2}$R	0.78	87	84.3	11.7	87.8	82.7	11.8
TS-L$_{0.4}$R	0.77	100	90.7	13.7	97.4	89.1	13.3
TS-L$_{0.4}$S	0.81	94.6	85.2	12.3	88.8	84.5	11.5
TS-L$_{0.6}$R	0.77	21.3	22.7	2.9	4.0	7.5	0.5

[a] Reaction conditions: 10 mL 500 ppm model fuels, 50 mg of material, n(TBHP)/n(sulphide) is 2, for 30min of the reaction at 60 °C. [b] Measured by ICP-OES. [c] Turnover number is defined as moles of converted DBT or 4,6-DMDBT at per mole of Ti sites.

Table S2 Comparison of catalytic performance over some representative hierarchical TS-1 catalysts for oxidation desulfurization of DBT

Catalyst	Ti wt.%	Cat. (mg)	S (ppm)	Oxidant [b]/S	Temp. (°C)	Conv.$_{\text{DBT}}$ (%)	TON[d]	Ref.
TS-L$_{0.4}$R	0.77	50	500	2	60	100	13.7	This work
HTS-1B	3.40[a]	50	500	2	60	40[c]	1.2[d]	4
HTS-1C	2.11[a]	50	500	2	60	45[c]	2.2[d]	5
TS-1C	2.00[a]	50	500	2	60	100[c]	5.3[d]	6
TS-1 (H3)	0.94[a]	55	500	2	60	100[c]	10.2[d]	7

[a] Ti content was calculated according to Si/Ti ratio; [b] Oxidant was TBHP, TBHP/S = 2; [c] reported data; [d] TON was calculated based on the conversion at 30 min reaction.

References

1. G. Xiong, Y. Cao, Z. Guo, Q. Jia, F. Tian and L. Liu, The roles of different titanium species in TS-1 zeolite in propylene epoxidation studied by in situ UV Raman spectroscopy, *Phys. Chem. Chem. Phys.*, 2016, **18**, 190-196.
2. L.-H. Chen, X.-Y. Li, G. Tian, Y. Li, J. Rooke, G.-S. Zhu, S.-L. Qiu, X.-Y. Yang and B.-L. Su, Highly stable and reusable multimodal zeolite TS-1 based catalysts with hierarchically interconnected three-level micro–meso–macroporous structure, *Angew. Chem. Int. Ed.*, 2011, **50**, 11156-11161.
3. T. Zhang, X. Chen, G. Chen, M. Chen, R. Bai, M. Jia and J. Yu, Synthesis of anatase-free nano-sized hierarchical TS-1 zeolites and their excellent catalytic performance in alkene epoxidation, *J. Mater. Chem. A*, 2018, **6**, 9473-9479.
4. S. Du, X. Chen, Q. Sun, N. Wang, M. J. Jia, V. Valtchev and J. Yu, A non-chemically selective top-down approach towards the preparation of hierarchical TS-1 zeolites with improved oxidative desulfurization catalytic performance, *Chem. Commun.*, 2016, **52**, 3580-3583.
5. S. Du, F. Li, Q. Sun, N. Wang, M. Jia and J. Yu, A green surfactant-assisted synthesis of hierarchical TS-1 zeolites with excellent catalytic properties for oxidative desulfurization, *Chem. Commun.*, 2016, **52**, 3368-3371.
6. S. Du, Q. Sun, N. Wang, X. Chen, M. Jia and J. Yu, Synthesis of hierarchical TS-1 zeolites with abundant and uniform intracrystalline mesopores and their highly efficient catalytic performance for oxidation desulfurization, *J. Mater. Chem. A*, 2017, **5**, 7992-7998.
7. R. Bai, Q. Sun, Y. Song, N. Wang, T. Zhang, F. Wang, Y. Zou, Z. Feng, S. Miao and J. Yu, Intermediate-crystallization promoted catalytic activity of titanosilicate zeolites, *J. Mater. Chem. A*, 2018, **6**, 8757-8762.