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Electronic Supplementary Information (ESI)

A non-chemically selective top-down approach to prepare hierarchical TS-1 zeolites with improved oxidative desulfurization catalytic performance

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A. Materials and Methods

The reagents used in this work include tetraethylorthosilicate (TEOS) (Beijing Chemical Works), (TBOT) (98%, tetrabutvl titanate Guangfu Fine Chemical Research Institute). tetrapropylammonium hydroxide (25 wt%, Shanghai Sharp Chemical Technology Co., LTD), H₂O₂ (30%, Beijing Chemical Works), tert-butyl hydroperoxide (65%, Sinopharm Chemical Reagent Co., LTD), n-octane (95%, Guangfu Fine Chemical Research Institute), dibenzothiophene (DBT) (98%, Shanghai Yu Kang Biotechnology Co., LTD), NaOH (96%, Beijing Chemical Works), HF (96%, Beijing Chemical Works), NH₄F (96%, Beijing Chemical Works), ethanol (99.8%, Beijing Chemical Works).

Synthesis of initial microporous TS-1 catalyst: Hydrothermal synthesis of TS-1: the initial TS-1 was synthesized from the starting gel with the optimized molar composition of SiO₂: 0.05TiO₂:0.27TPAOH:124H₂O by using tetrapropylammonium hydroxide (TPAOH, 25 wt%) as the template for micropores. Typically, TPAOH and the deionized water were firstly mixed completely, then the mixture of TEOS and TBOT were added dropwise to the above mixed solution, further strirred for 10 h to allow a full hydrolysis of TEOS and TBOT. Finally, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 180 °C for 2 days under static conditions. The assynthesized solid product was separated by high speed centrifugation, washed thoroughly with deionized water and ethanol, and then dried over night at 80 °C in the oven overnight.

Preparation of hierarchical TS-1:

The as-synthesized TS-1 crystals were used for the preparation of hierarchical materials. Hierarchical TS-1 crystals were achieved by using two different fluoride chemical etching post-treated routes.

- 1. HF+NH₄F route: The treatment was carried with HF-NH₄F mixed aqueous solution. The etching solution was prepared by mixing 36.0 mL of 0.1 M HF solution with a mixture of 0.36 g of NH₄F and 36.0 g of H₂O. 0.6 g of as-synthesized TS-1 crystals were subjected to treatment at 25 °C for 15 min under ultrasonic radiation. The final product was separated by high speed centrifugation. The resulting sample was denoted as HTS-1A.
- 2. NaOH+HF+NH₄F route: A consecutive treatment with 1M NaOH aqueous solutions and HF-NH₄F mixed aqueous solution, was performed. 0.6 g of as-synthesized TS-1 crystals were firstly treated using 40 ml of 1M NaOH with stirring at room temperature for 15 min. The solid was separated by high speed centrifugation, washed and dried. Subsequently, the obtained solid was subjected to HF-NH₄F mixture treatment at 25 °C for 15 min under ultrasonic radiation. The fluoride etching solution was prepared by mixing 36.0 mL of 0.1 M HF solution with a mixture of 0.36 g of NH₄F and 36.0 g of H₂O. The final product was separated by high speed centrifugation, washed and dried. The resulting sample was denoted as HTS-1B.

All samples were thoroughly washed with distilled water. The resulting hierarchical TS-1 samples were dried overnight at 80 °C and calcined at 550 °C for 6 h.

B. Characterizations:

The crystallinity and phase purity of the samples were analized by power X-ray diffraction (XRD) analysis on a Rigaku D-Max 2550 diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å). The crystal size and morphology were determined 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. Infrared spectra (IR) were recorded by Nicolet Impact 410 FTIR Infrared Instrument using KBr pellet technique. The UV-Vis DRS (diffuse reflectance spectroscopy) of the catalysts were recorded over the range of 200 nm to 800 nm against the support as reference, on a SHIMADZU U-4100. Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77.3 K after degassing of the samples at 350 °C under vacuum. Chemical compositions were determined with inductively coupled plasma (ICP) analyses carried out on a Perkin-Elmer Optima 3300 DV ICP instrument.

C. Catalytic tests

The oxidation of dibenzothiophene (DBT): 0.6g dibenzothiophene (DBT) was dissolved in 200 ml n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 ml three neck glass flask with an oil-heating bath under vigorous stirring (650 rap/min). In a standard run, 10 ml of model fuel and 50 mg of catalyst were added to the reactor. *Tert*-butylhydroperoxide (TBHP) was used as oxidant, and the molar ratio of TBHP/DBT was 2. The reaction was carried at 333 K for 3-6 h. The oil phase was analyzed periodically on a chromatograph (GC-126 of INESA ANALYTICAL INSTRUMENT CO., LTDD), equipped with a flame photometric detector (FPD) and HP-5 capillary column (Agilent J&W GC Columns, φ 0.25 mm × φ 0.32 mm × 30 m). The reaction scheme of the DBT oxidation to yield the corresponding sulphone is following:



The removal rate (R) of sulfur compounds is expressed as:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

 C_0 is the initial mass concentration of sulfur compounds and C_t is the mass concentration after reacting *t* hour.

E. Supplementary Figures and Tables



Fig. S1 DFT pore size distribution curves of parent TS-1 (a and b) and the samples subjected to: treatment with NH_4F -HF (c and d) and consecutive treatment with NaOH and NH_4F -HF solutions (e and f).



Fig. S2 XRD patterns of the parent (TS-1) and the hierarchical (HTS-1A and HTS-1B) materials.



Fig. S3 SEM images of parent TS-1 (a, b) and the hierarchical HTS-1A (c, d) and HTS-1B (e, f) samples.



Fig. S4 FT-IR spectra of initial TS-1 and the hierarchical samples obtained by different treatment procedures.



Fig. S5 Recycle tests in the oxidation of DBT using the hierarchical HTS-1B catalyst recovered by centrifugation and drying at 80 °C.



Fig. S6 Recycle tests in the oxidation of DBT using the regenerated HTS-1B catalyst. Reaction time 4 h; regeration temperature 550°C.



Fig. S7 FT-IR spectra of initial, recovered by centrifugation and drying at 80°C and regenerated by calcination at 550°C HTS-1B catalyst. The reference spectra of DBT and DBTO are included in the figure.



Fig. S8 UV spectra of of initial, recovered by centrifugation and drying at 80°C and regenerated by calcination at 550°C HTS-1B catalyst.

Table 51 DBT oxidation over parent 15-1 and merarchical 15-1 catalysis.									
Catalyst	Sulfur concentration	DBT Conversion/%							
	before reaction (ppm)	0h	1h	2h	3h	4h	5h	6h	
TS-1	500	0	10.4	37.6	36.6	36.4	36.1	36.5	
HTS-1A ^a	500	0	67.5	88.5	92.8	93.1	94.4	94.0	
HTS-1B ^b	500	0	69.6	86.3	93.2	100.0	100.0	100.0	

Table S1 DBT oxidation over parent TS-1 and hierarchical TS-1 catalysts.

Reaction conditions: 10 ml 500 ppm model fuel, catalyst=50 mg, T=333 K, oxidant/s-organic = 2 (molar ratio).

^a Parent TS-1 treated with NH₄F-HF aqueous solution.

^b Parent TS-1 treated with NaOH and a mixture of NH₄F-HF aqueous solution.

Table S2 Recycle tests in the DBT oxidation over hierarchical TS-1B catalyst.

Recycle	Sulfur concentration	DBT Conversion/%							
Times	before reaction (ppm)	0h	1h	2h	3h	4h	5h	6h	
0	500	0	69.6	86.3	93.2	100.0	100.0	100.0	
1	500	0	47.8	52.2	59.4	60.0	61.6	63.5	
2	500	0	33.0	31.3	33.1	33.5	33.5	33.7	
3	500	0	19.0	34.2	35.8	37.8	37.4	40.8	

Reaction conditions: 10 ml 500 ppm model fuel, catalyst=50 mg, T=333 K, oxidant/s-organic = 2 (molar ratio).