

Electronic Supplementary Material (ES) for ChemComm  
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## **Electronic Supplementary Information (ESI)**

### **A green surfactant-assisted synthesis of hierarchical TS-1 zeolites with excellent catalytic properties for oxidative desulfurization**

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## A. Materials and Methods

The reagents used in this work include tetraethylorthosilicate (TEOS) (Beijing Chemical Works), tetrabutyl titanate (TBOT) (98%, Guangfu Fine Chemical Research Institute), tetrapropylammonium hydroxide (25 wt %, Shanghai Sharp Chemical Technology Co., LTD), H<sub>2</sub>O<sub>2</sub> (30%, Beijing Chemical Works), tert-butyl hydroperoxide (65%, Sinopharm Chemical Reagent Co., LTD), ethanol (99.8%, Beijing Chemical Works), n-octane (95%, Guangfu Fine Chemical research institute), thiophene (Th) (99.94%, Guangfu Fine Chemical Research Institute), dibenzothiophene (DBT) (98%, Shanghai Yu Kang Biotechnology Co., LTD), Triton X-100 (Polyethylene glycol tert-octylphenyl ether, Aladdin, the molecular of Triton X-100 is C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH (n=10)), benzothiophene (BT) (99%, Energy Chemical), 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) (99%, Energy Chemical).

**Synthesis of Hierarchically porous TS-1 catalysts (HTS-1A, HTS-1B and HTS-1C):** The hierarchically porous TS-1 catalysts (HTS-1A, HTS-1B and HTS-1C) were synthesized from the starting gels with the optimized molar compositions of SiO<sub>2</sub>: 0.033TiO<sub>2</sub>: 0.2TPAOH: 1.5CH<sub>3</sub>CH<sub>2</sub>OH: 9H<sub>2</sub>O: nTriton X-100 (n = 0.102, 0.204 and 0.408) under hydrothermal conditions at 170 °C by using tetrapropylammonium hydroxide (TPAOH) as the template for micropores and Triton X-100 for mesopores. Typically, TPAOH (25 wt%) and deionized water were mixed completely, then TEOS was dropwised to a mixture of H<sub>2</sub>O and TPAOH under vigorous stirring for 8 h, the final product was a clear solution (solution A). Tetrabutyl orthotitanate (TBOT) was dissolved into ethanol (solution B). Then solution B was added to solution A dropwise. After being strided into the solution and hydrolyzed for about 4 h at room temperature. In order to promote the protozeolitic units generation, the solution was stirred in a reflux system conditions at 90 °C for 24 h. Under string, the Triton X-100 was added to the mixture. The resulting solution was stirred at 90 °C for another 6 h, then transferred into a 100 ml Teflon-lined stainless steel autoclave. Finally, the crystallization treatment was carried out in a conventional oven at 170 °C for 4 d under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 6 h.

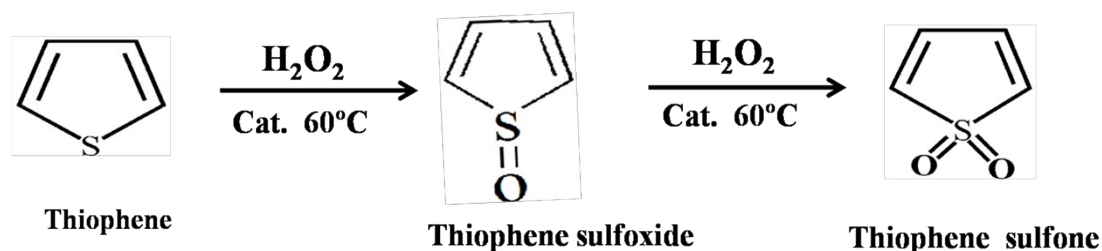
**Conventional microporous TS-1 catalyst (TS-1) :** The conventional microporous TS-1 catalyst (TS-1) was synthesized from the starting gel with the optimized molar composition of SiO<sub>2</sub>: 0.033TiO<sub>2</sub>: 0.2TPAOH: 1.5CH<sub>3</sub>CH<sub>2</sub>OH: 9H<sub>2</sub>O under hydrothermal conditions at 170 °C by using tetrapropylammonium hydroxide (TPAOH) as the template for micropores. Typically, TPAOH and deionized water were mixed completely, then TEOS was dropwised to a mixture of H<sub>2</sub>O and TPAOH under vigorous stirring for 8 h, the final product was a clear solution (solution A). Tetrabutyl orthotitanate (TBOT) was dissolved into ethanol (solution B). Then solution B was added to solution A dropwise. After being strided into the solution and hydrolyzed for about 4 h at room temperature. In order to promote the protozeolitic units generation, the solution was stirred in a reflux system conditions at 90 °C for 24 h, then transferred into a 100 ml Teflon-lined stainless steel autoclave. Finally, the crystallization treatment was carried out in a conventional oven at 170 °C for 4d under static conditions. The as-synthesized solid products were centrifuged, wished with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 6 h.

## B.Characterizations:

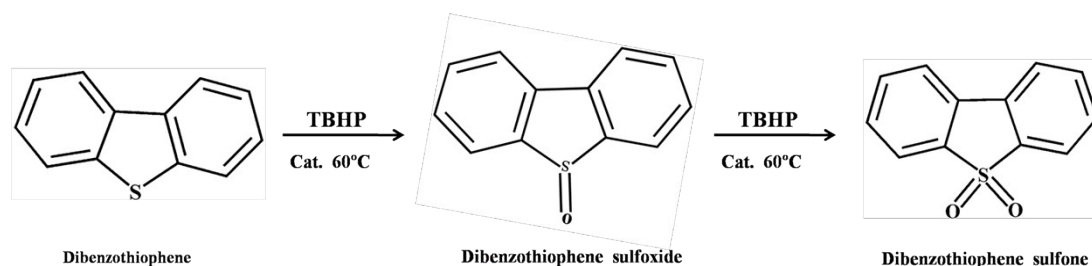
The crystallinity and phase purity of the samples were characterized by power X-ray diffraction (XRD) on a Rigaku D-Max 2550 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The crystal size and morphology were measured by a scanning electron microscopy (SEM) using a JSM-6700F (JEOL) electron microscope. Transmission electron microscopy (TEM) images were recorded with a Tecnai F20 electron microscope. Chemical compositions were determined with an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS). 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 catalyst was recorded over the range of 200 nm to 800 nm against the support as reference, on a SHIMADZU U-4100. Argon adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 87.3 K after the samples were degassed at 160 °C under vacuum, The oxidized products were analyzed by Gas chromatography-Mass spectrometry (GC-MS) (Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60m  $\times$  320 $\mu$ m  $\times$  25 $\mu$ m ).

## C. Catalytic tests

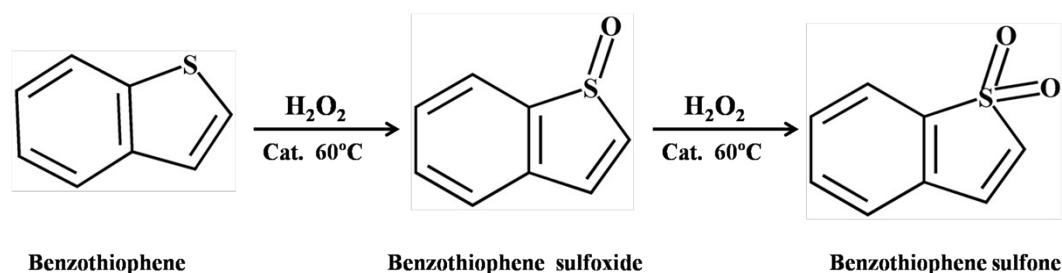
**The oxidation of Th:** A certain amount of Th was dissolved in n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 ml three neck glass flask with an oil-heating bath under vigorous stirring (600 rap / min). In a standard run, 10 ml of model fuel, 10 ml H<sub>2</sub>O, and 50 mg of catalyst were added to the reactor. H<sub>2</sub>O<sub>2</sub> (30 wt %) was used as oxidant, and the molar ratio of H<sub>2</sub>O<sub>2</sub>/Th 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,  $\phi$  0.25 mm  $\times$   $\phi$  0.32 mm  $\times$  30 m). The simplified reaction of Th oxidation is following:



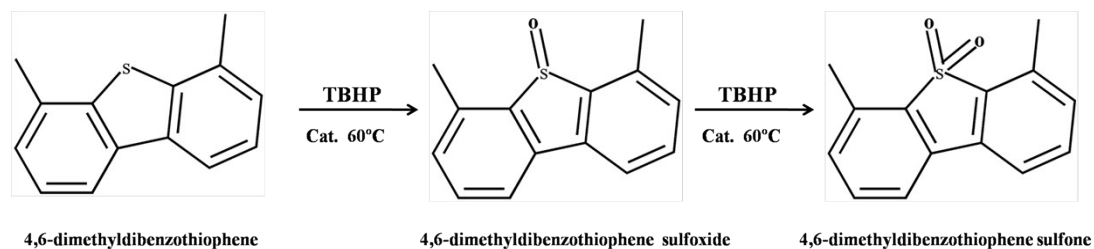
**The oxidation of DBT:** A certain amount of DBT was dissolved in n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 ml three neck glass flask with an oil-heating bath under vigorous stirring (600 rap / min). In a standard 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,  $\phi$  0.25 mm  $\times$   $\phi$  0.32 mm  $\times$  30 m). The simplified reaction of DBT oxidation is following:



**The oxidation of BT:** A certain amount of BT was dissolved in 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 (600 rap / min). In a standard run, 10 ml of model fuel, 10 ml CH<sub>3</sub>OH, and 50 mg of catalyst were added to the reactor. H<sub>2</sub>O<sub>2</sub> (30 wt %) was used as oxidant, and the molar ratio of H<sub>2</sub>O<sub>2</sub>/BT 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 simplified reaction of BT oxidation is following:



**The oxidation of 4, 6-DMDBT:** A certain amount of 4, 6-DMDBT was dissolved in 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 (600 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/4, 6-DMDBT 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 simplified reaction of 4, 6-DMDBT oxidation is following:

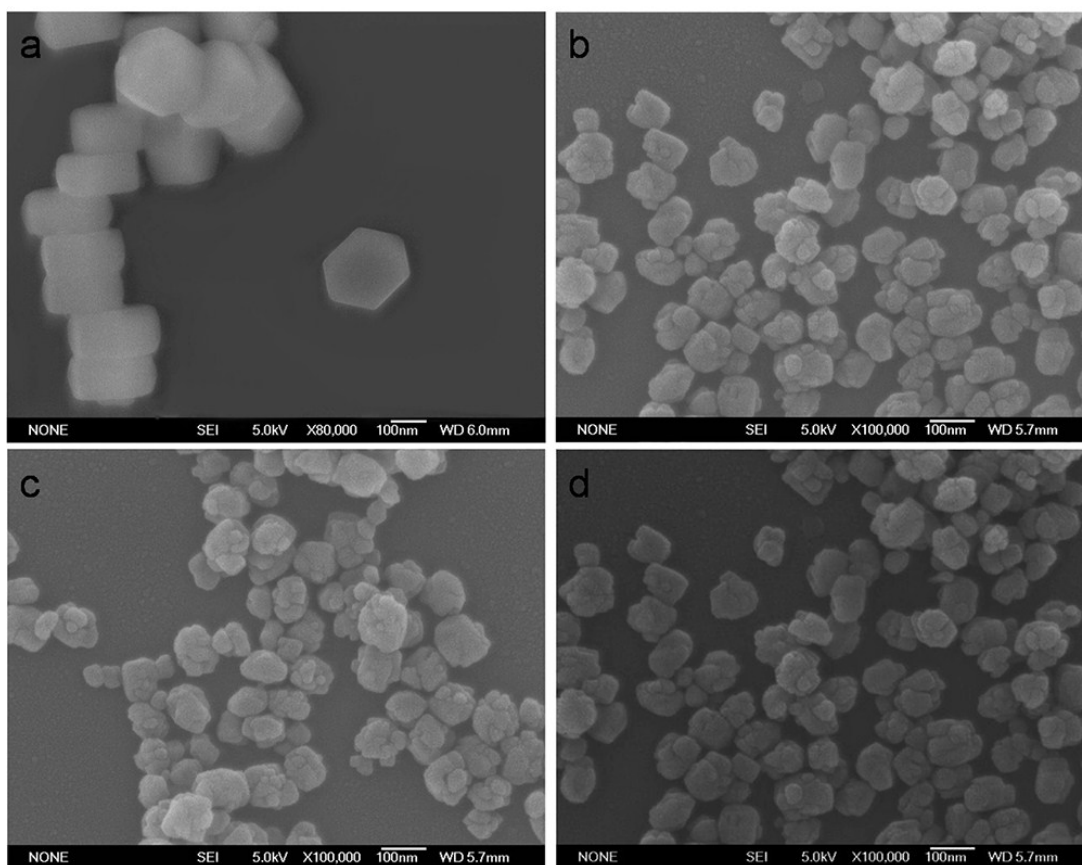


The removal rate (R) of sulfur compounds is expressed as:

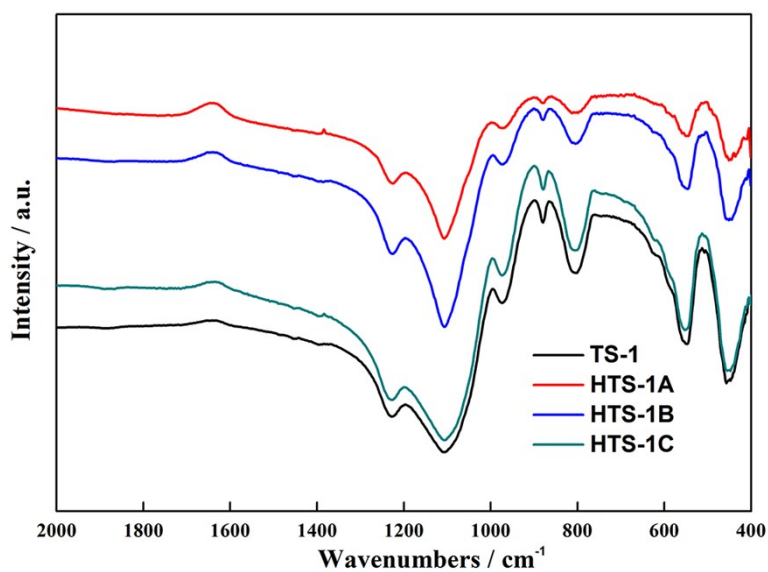
$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

$C_0$  is the initial mass concentration of sulfur compounds and  $C_t$  is the mass concentration after reacting  $t$  h.

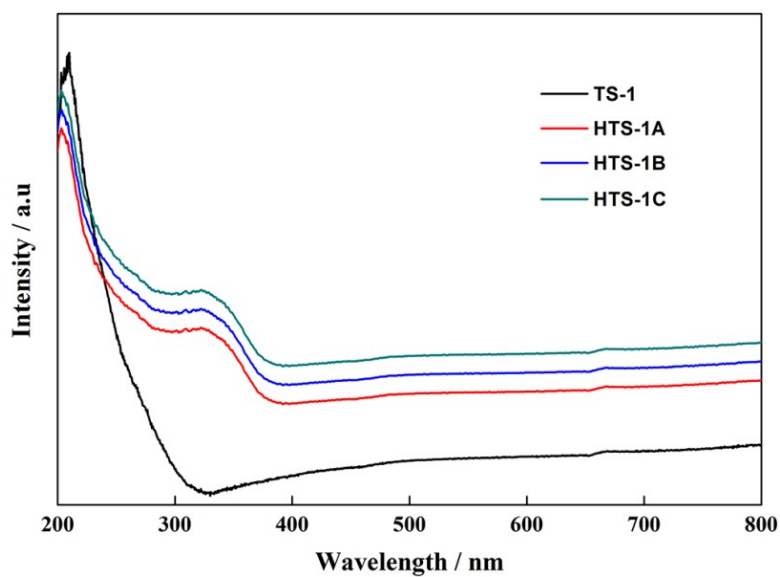
#### D. Supplementary Figures and Tables



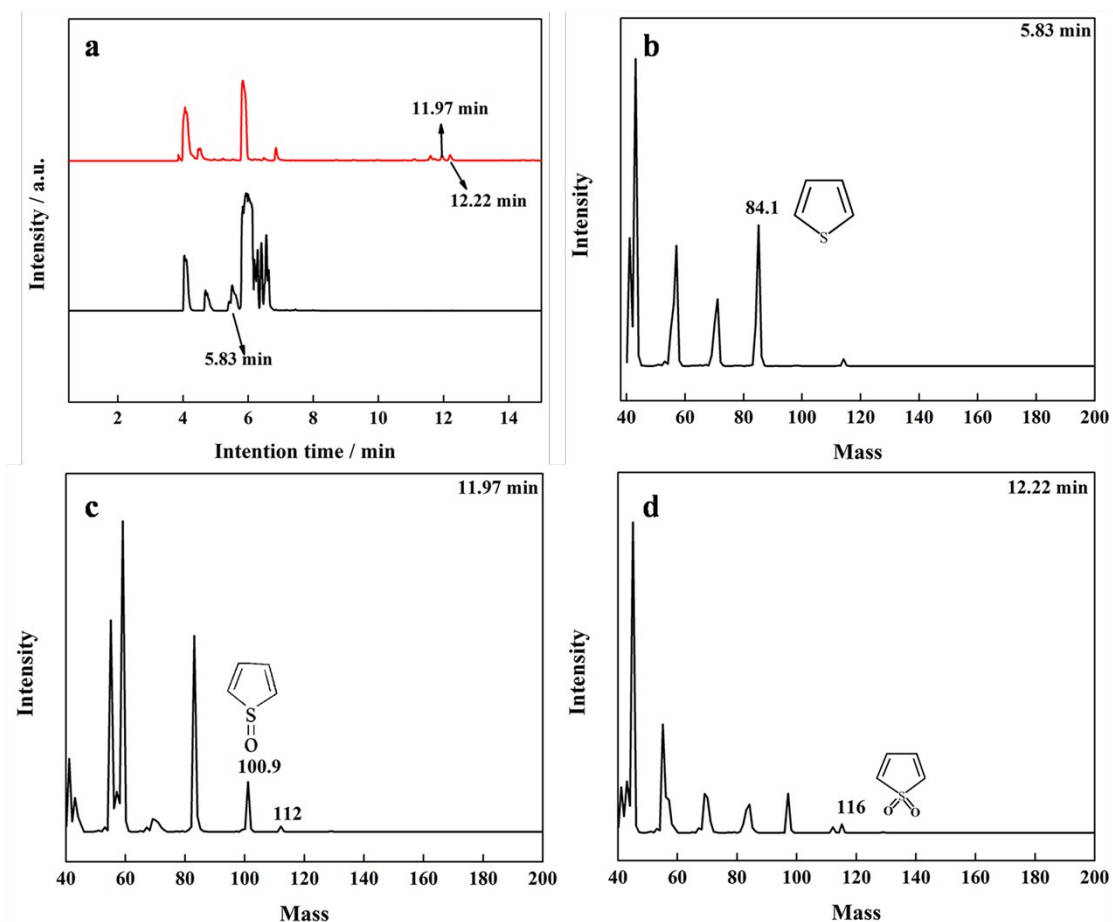
**Fig. S1** SEM images of conventional microporous TS-1 (a) and hierarchically porous HTS-1A (b), HTS-1B (c) and HTS-1C (d)



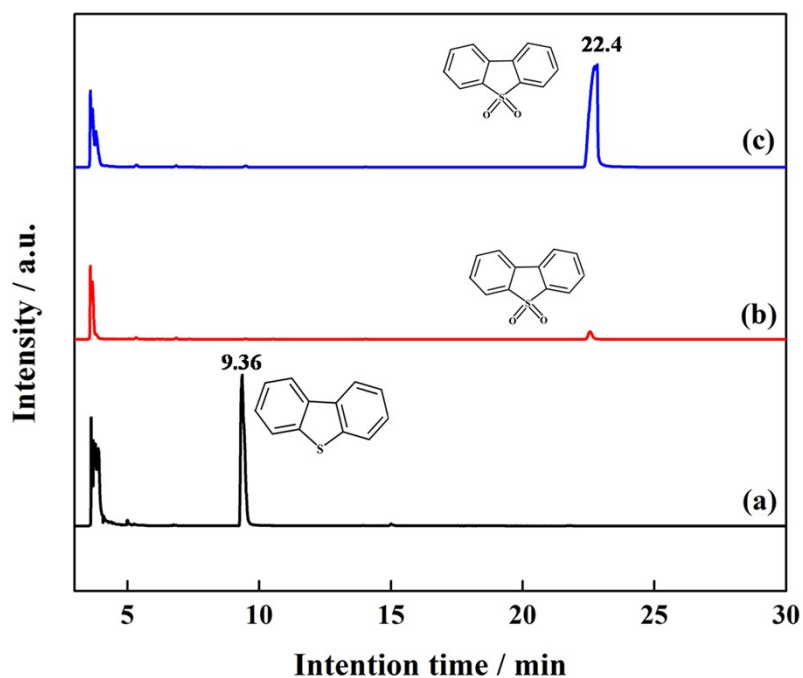
**Fig. S2** FT-IR spectra of conventional microporous TS-1 and hierarchically porous TS-1



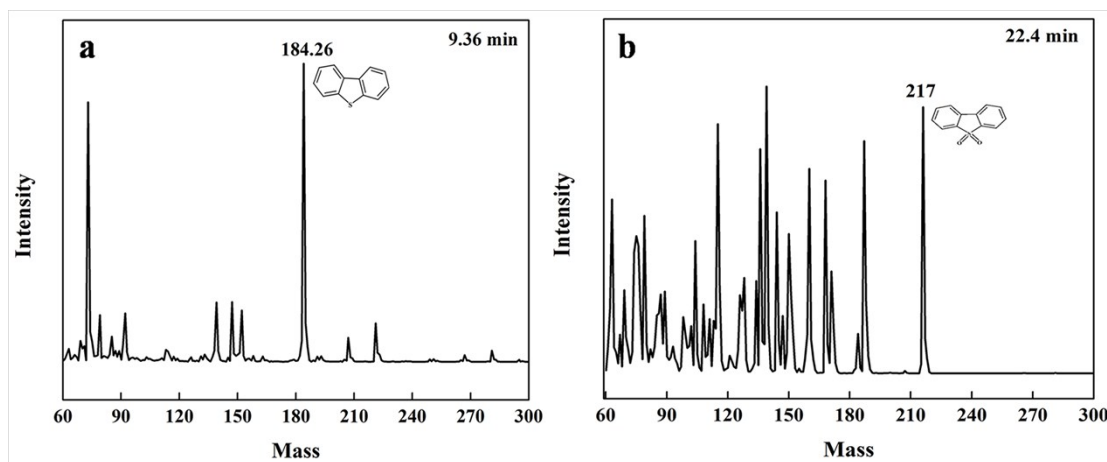
**Fig. S3** UV spectra of conventional microporous TS-1 and hierarchically porous TS-1



**Fig. S4** GC-MS chromatograms of oxidation of Th. The structures annotated onto the chromatograms are identified by the molecular weight given in the mass spectra. (a) The chromatograms spectra of before reaction and after reaction; (b) The Mass spectra of Th; (c) The Mass spectra of the products (thiophene sulfoxide); (d) The Mass spectra of the products (thiophene sulfone)

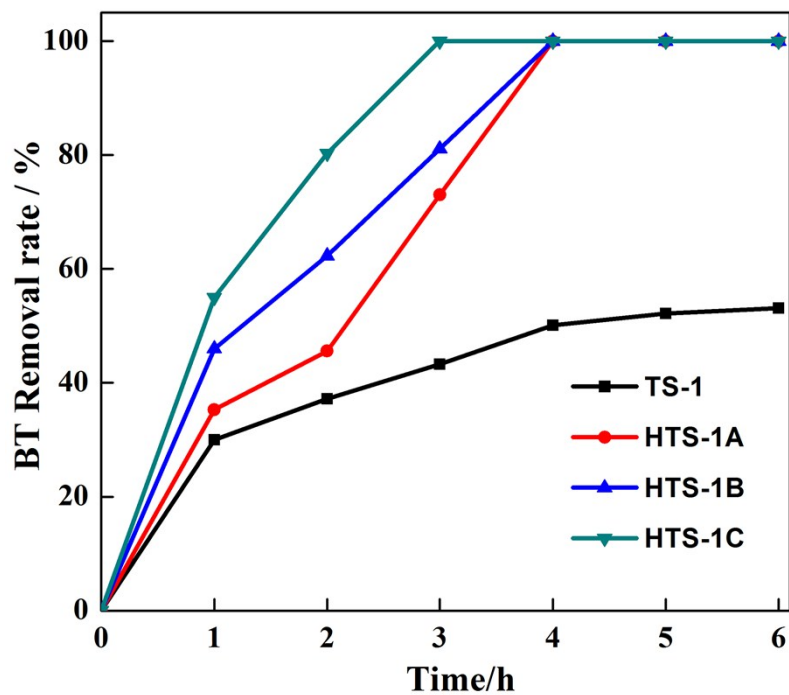


**Fig. S5** GC-MS chromatograms of oxidation of DBT. The structures annotated onto the chromatograms are identified by the standard mass spectra in the NIST database. (a) The chromatograms spectra of before reaction; (b) The chromatograms spectra of after reaction; (c) The chromatograms spectra of the acetone as solvent used for extracting adsorbed dibenzothiophene sulfone from used catalyst.

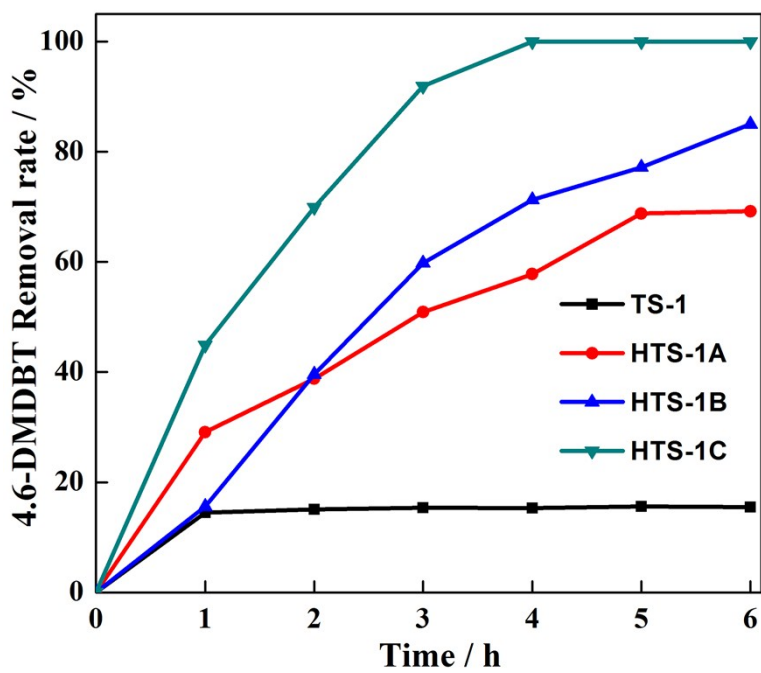


**Fig. S6** The Mass spectra of dibenzothiophene (DBT) and dibenzothiophene sulfone; (a) The Mass spectra of the dibenzothiophene (DBT); (b) The Mass spectra of the products (dibenzothiophene sulfone)

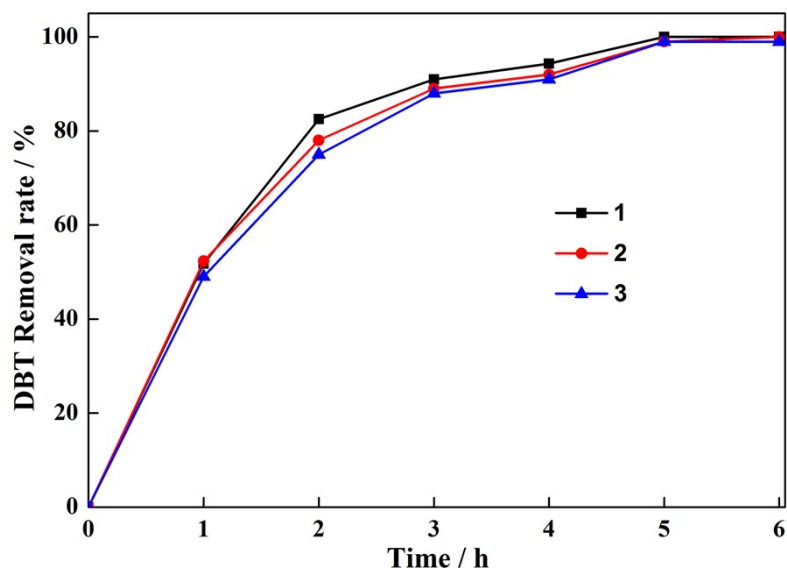




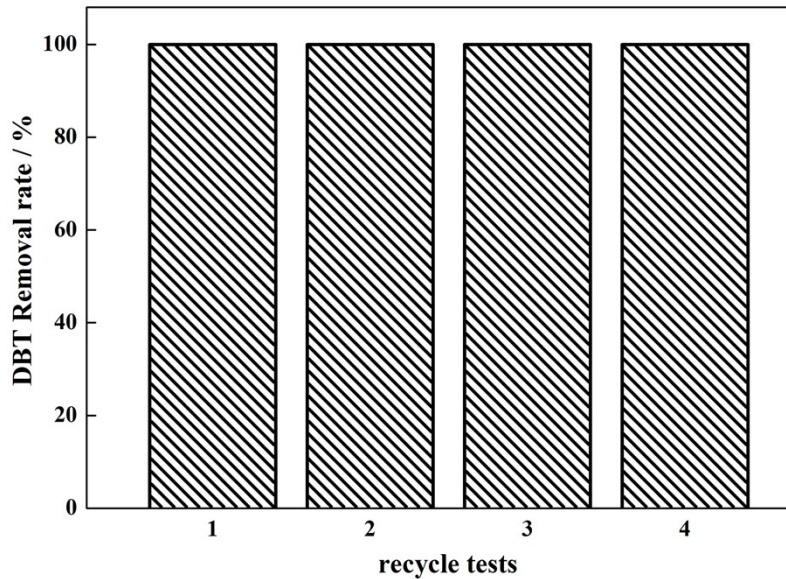
**Fig. S7** Oxidation of BT over hierarchically porous TS-1 and conventional TS-1 zeolites



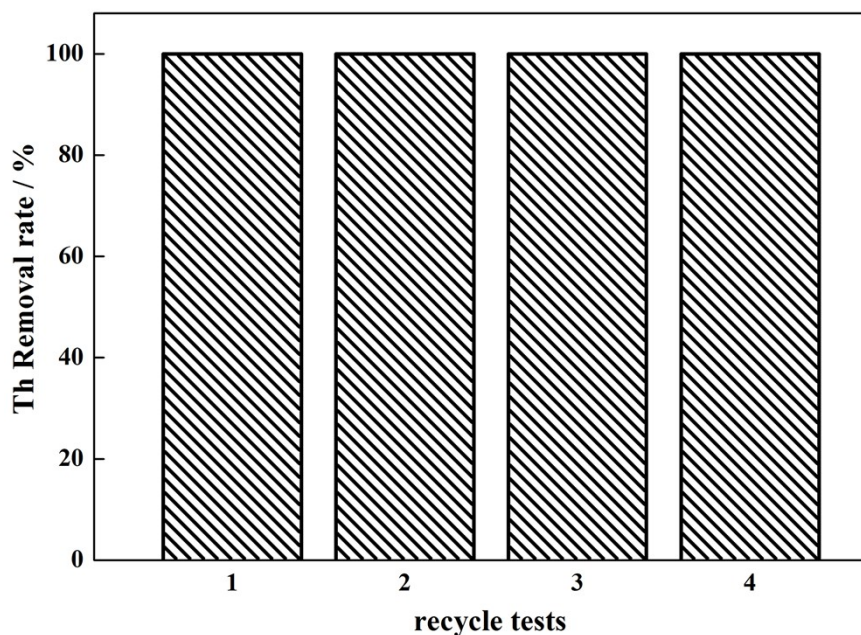
**Fig. S8** Oxidation of 4, 6 - DMDBT over hierarchically porous TS-1 and conventional TS-1 zeolites



**Fig. S9** Recycle tests in the oxidation of DBT using the regenerated HTS-1A upon calcination at 550 °C as the catalyst



**Fig. S10** Recycle tests in the oxidation of DBT using the regenerated HTS-1A upon calcination at 550 °C as the catalyst ( reaction time = 6h )



**Fig. S11** Recycle tests in the oxidation of Th using the regenerated HTS-1A upon calcination at 550 °C as the catalyst ( reaction time = 3h )

Table S1 The DBT oxidation over conventional microporous TS-1 and hierarchially porous HTS-1A, HTS-1B and HTS-1C

Catalyst	Sulfur concentration before reaction(ppm)	DBT Removal rate /%						
		0h	1h	2h	3h	4h	5h	6h
TS-1	500	0	25.3	44.0	60.6	70.7	70.7	70.8
HTS-1A	500	0	51.8	82.5	91.0	94.3	97.6	99.0
HTS-1B	500	0	58.9	87.8	100.0	100.0	100.0	100.0
HTS-1C	500	0	85.0	95.0	100.0	100.0	100.0	100.0

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

Table S2 The recycle tests in the DBT oxidation over hierarchially porous HTS-1A

Recycle Times	Sulfur concentration before reaction(ppm)	DBT Removal rate /%						
		0h	1h	2h	3h	4h	5h	6h
1	500	0	51.8	82.5	91.0	94.3	97.6	99.0
2	500	0	52.3	78.0	89.0	92.0	98.0	98.5
3	500	0	49.0	75.0	88.0	91.0	99.0	99.0

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

Table S3 The Th oxidation over conventional microporous TS-1 and hierarchially porous HTS-1A, HTS-1B and HTS-1C

Catalyst	Sulfur concentration befor reaction(ppm)	Th Removal rate /%						
		0h	1h	2h	3h	4h	5h	6h
TS-1	500	0	26.2	37.5	44.5	53.0	66.6	77.1
HTS-1A	500	0	78.4	95.2	100.0	100.0	100.0	100.0
HTS-1B	500	0	94.0	100.0	100.0	100.0	100.0	100.0
HTS-1C	500	0	98.0	100.0	100.0	100.0	100.0	100.0

Reaction conditions: 10 ml 500 ppm model fuel, 10 ml H<sub>2</sub>O, catalyst=50 mg, T=333K, oxidant/ S-containing organic = 2 (molar ratio)

Table S4 The BT oxidation over conventional microporous TS-1 and hierarchially porous HTS-1A, HTS-1B and HTS-1C

Catalyst	Sulfur concentration befor reaction(ppm)	BT Removal rate /%						
		0h	1h	2h	3h	4h	5h	6h
TS-1	500	0	30.0	37.2	43.3	50.1	52.2	53.1
HTS-1A	500	0	35.3	45.6	73.0	100.0	100.0	100.0
HTS-1B	500	0	46.0	62.3	81.1	100.0	100.0	100.0
HTS-1C	500	0	55.0	80.3	100.0	100.0	100.0	100.0

Reaction conditions: 10 ml 500 ppm model fuel, 10 ml CH<sub>3</sub>OH, catalyst=50 mg, T=333 K, oxidant/ S-containing organic = 2 (molar ratio)

Table S5 The 4, 6 - DMDBT oxidation over conventional microporous TS-1 and hierarchially porous HTS-1A, HTS-1B and HTS-1C

Catalyst	Sulfur concentration befor reaction(ppm)	4, 6 - DMDBT Removal rate /%						
		0h	1h	2h	3h	4h	5h	6h
TS-1	500	0	14.5	15.1	15.4	15.3	15.6	15.1
HTS-1A	500	0	29.1	38.8	50.9	57.8	68.8	69.2
HTS-1B	500	0	15.6	39.6	59.8	71.3	77.2	85.0
HTS-1C	500	0	44.9	69.9	91.9	100.0	100.0	100.0

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