

## Supporting information

### Experimental Section

#### 1. Chemicals.

Tetraethyl orthosilicate (TEOS, Shanghai Lingfeng Chemical Co., China), tetrabutyl orthotitanate (TBOT, Acros organics), tetrapropylammonium hydroxide (TPAOH, 25 wt.% in water, Yixing Dahua Chemical Co., China), cetyltrimethylammonium bromide (CTAB) and isopropanol (IPA) were obtained from Sinopharm chemical Reagent Co., China. Thiophene was purchased from Tokyo chemical industry Co., Ltd (TCI). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35 wt.% in water) were purchased from Acros organics. *tert*-Butanol (TBOH, Amethyst chemicals) and *n*-Octane were obtained from Sinopharm chemical Reagent Co., China. Absolute ethylalcohol, deionized water and all the other chemicals above were used as received without any purification.

#### 2. Characterization.

X-ray diffraction patterns were obtained with a Rigaku D/Max 2200PC diffractometer using Cu K $\alpha$  radiation (40 kV and 40 mA) with a scanning rate of 4° min<sup>-1</sup> for detection. FTIR spectra were recorded in the range of 400 – 4000 cm<sup>-1</sup> using a Nicolet 7000-C at a resolution of 8 cm<sup>-1</sup>, at room temperature and at 350 °C (623K), respectively. UV-VIS spectra were recorded from 190 to 800 nm on the Shimadzu UV-310PC spectrometer with BaSO<sub>4</sub> as a reference. The TEM images were taken with a JEOL-2010F electron microscope operated at 200 kV. FE-SEM (Field Emission Scanning Electron Microscope) images were obtained on FEI-Magellan 400L. The concentration of Ti in zeolites and reaction solutions after catalysts separation, were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). N<sub>2</sub> adsorption desorption isotherms were performed at 77K with Micrometrics Tristar 3000. The specific surface area and the pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively, while the micropore volume and external surface area of samples were calculated according to the *t*-plot method. Catalysts deactivation were investigated by performing TG-MS analysis of samples

after three cycles reaction on Netzsch STA 409 F3 and QMS 403, at a heating rate of 10 K/min under N<sub>2</sub>/O<sub>2</sub> atmosphere (oxygen flow rate of 20 mL/min and nitrogen flow rate of 10 mL/min).

### **3. Synthesis of mesoporous TS-1 zeolites (MTS-1), and traditional TS-1 zeolites.**

TEOS (15.624 g) were mixed with 36 g deionized water followed by the addition of TPAOH (10.98 g, 25 wt%). The mixture became clear after stirring at room temperature for 3-5 h. Meanwhile, by dissolving 0.5090 g tetrabutyl orthotitanate (TBOT) in 10 g isopropanol (IPA), the hydrolysis rate of TBOT slowed down. Then, the titanium source was added slowly into the silicon mixture at 5 °C and kept stirring at this temperature for 12 h to prevent the formation of isolated TiO<sub>x</sub> phase. The mixture became clear solution after stirring at 40 °C for another 8-12 h and this process ensure the incorporation of Ti into silicon tetrahedron. After aging at 90 °C for 6 h, zeolite nanoparticles came into formation, which were then interacted with surfactant solutions (1.8 g CTAB dissolved in 150 g deionized water ). The final mixture was kept stirring at room temperature for 6-8 h, and 30 g ethanol was added into the mixture before transferred into Teflon-lined stainless steel autoclaves for hydrothermal treatment under autogenous pressure at 150 °C for 15 h. Samples were separated by high speed centrifugation at 10000 r/min, washed with deionized water repeatedly for three times, dried overnight at 100 °C, calcined at 600°C for 7 h, and labeled as mesoporous TS-1 zeolites (MTS-1). And the final composition recipe was TBOT: TEOS: TPAOH: CTAB: IPA: EtOH: H<sub>2</sub>O= 1: 50: 9: 3.26: 110: 435: 7193.

Traditional TS-1 zeolites were prepared by hydrothermal treatment of zeolite precursor without any addition of CTAB. Zeolite precursor comprise 15.624 g TEOS, 186 g deionized water and 10.98 g TPAOH (25 wt%) as silicon source, and, 0.5090 g tetrabutyl orthotitanate (TBOT) in 10 g isopropanol (IPA) as titanium source. After the addition of titanium source into silicon source at 5 °C, zeolite precursor were kept stirring at room temperature till the mixture is clear, followed by direct hydrothermal treatment at 150 °C for 24 h. Samples were separated, calcined and designated as TS-1 zeolites, with other conditions unchanged.

### **4. Catalytic tests**

The reaction was performed in a three neck glass flask equipped with a condenser and a magnetic stirrer. An amount of sulfur compound (20  $\mu\text{L}$  thiophene) was added into 10 mL *n*-octane to act as model fuel, respectively, with the concentration of sulfur atom in simulated fuel about 800 ppm. 50 mg catalysts (MTS-1 and TS-1), 10 mL solvent (water or *tert*-butanol) and 42.9  $\mu\text{L}$   $\text{H}_2\text{O}_2$  (50 mmol, 35 wt %) as oxidant were then added into the reactor. The reaction was carried out at 333 K for different reaction time.

Thiophene Conversion is defined as:  $\frac{C_0 - C_t}{C_0} \times 100\%$ , where  $C_0$  is the initial molar concentration of thiophene in organic phase, and  $C_t$  is the molar concentration of thiophene in organic phase after reaction for  $t$  h. GC-MS data were used to calculate the conversion ratio through periodically analyzing oil phase by using cyclohexane as internal standard. Due to the strong peak of *n*-octane in GC spectrum, the data collected before the retention time point of *n*-octane were used for integration in calculating the conversion ratio. Hence, the calculation of conversion is based on the loss of thiophene from organic phase during reaction. For water as solvents, the reaction is a triphase system (S-L-L) which contain solid (catalysts), organic layer and aqueous phase, and only organic phase was analyzed periodically by GC-MS. For *tert*-butanol as solvent, which is a two-phase system, the organic phase is homogeneous, and analyzed to calculate the conversion of sulfur compounds.

Recycling tests were operated by the direct addition of 20  $\mu\text{L}$  thiophene and 42.9  $\mu\text{L}$   $\text{H}_2\text{O}_2$  into the reacting system, without catalysts separation and recalcination. Unreacted thiophene during the last test was considered in the calculation of conversion in recycling tests. After two recycles the deactivation of traditional TS-1 zeolites is obvious and thus, catalysts were separated from the reacting system for TG-MS analysis.

The presence of sulfate in water phase was testified by  $\text{BaCl}_2$  titration. First, MTS-1 catalysts were separated from reacting system through high speed centrifugation. Then 0.10 mol/L  $\text{BaCl}_2$  was added slowly into the liquid phase, and white precipitate took into formation which were separated through centrifugation,

dried and determined through XRD analysis as illustrated in the following Figure S6. The diffraction peaks of oxidized products after interaction with  $\text{BaCl}_2$  coincide with the standard data of  $\text{BaSO}_4$  (JCPDS card no.24-1035). Hence, the oxidation products of thiophene are sulfate.

In the oxidation of benzothiophene (BT), or dibenzothiophene (DBT), acetonitrile were used as solvents, and sulfur content were kept at 800 ppm, with other conditions unchanged. However, acetonitrile as solvent could extract sulfur compound from apolar phase into polar phase, thus, samples were taken respectively from each phase and the sulfur conversion is based on the oxidation without considering the contribution by solvent extraction.

**Figures:**

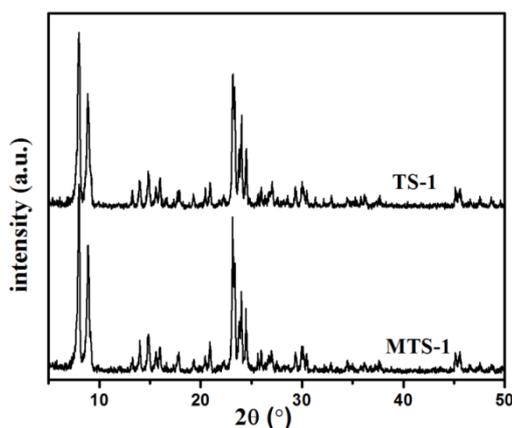


Figure S1. XRD patterns of traditional TS-1 zeolites (A) and mesoporous TS-1 zeolites (B).

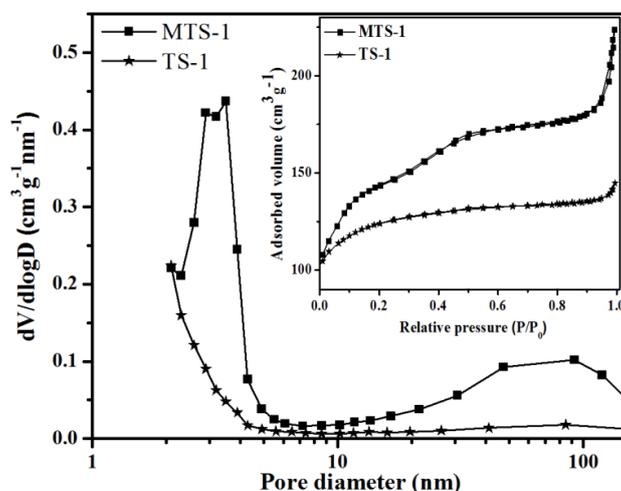


Figure S2. The BJH pore size distribution of traditional TS-1 zeolites (TS-1) and mesoporous

TS-1 zeolites (MTS-1), the insert is the corresponding nitrogen adsorption-desorption isotherms.

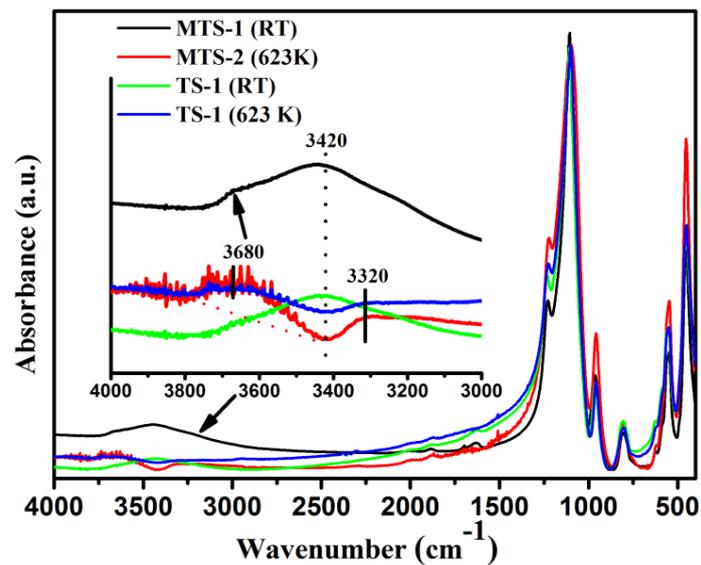


Figure S3. FT-IR spectra of traditional TS-1 zeolites, mesoporous TS-1 zeolites (MTS-1), collected at room temperature (designated as RT) and 350 °C (labelled as 623K), respectively.

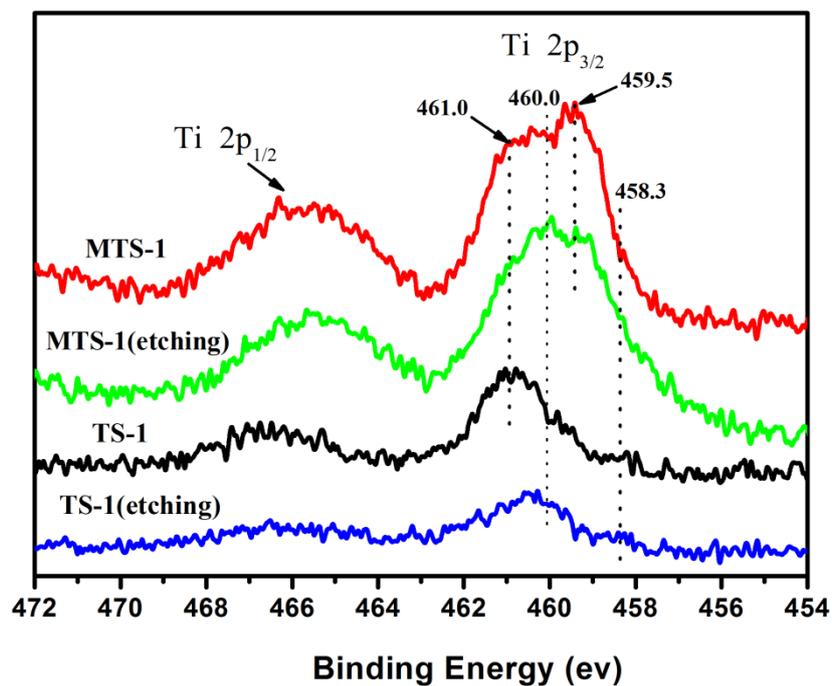


Figure S4. Ti 2p XPS of MTS-1 and TS-1 zeolites.

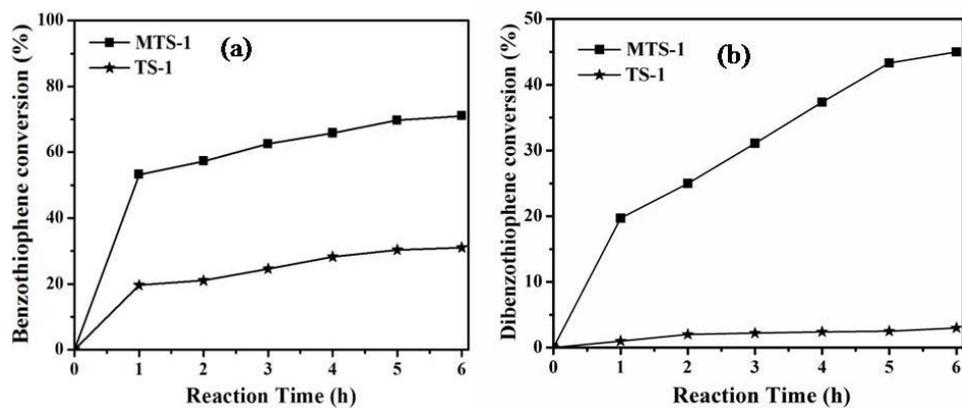


Figure S5. Oxidative conversion of benzothiophene (a), and dibenzothiophene (b), over TS-1 and MTS-1 catalysts by using acetonitrile as solvents

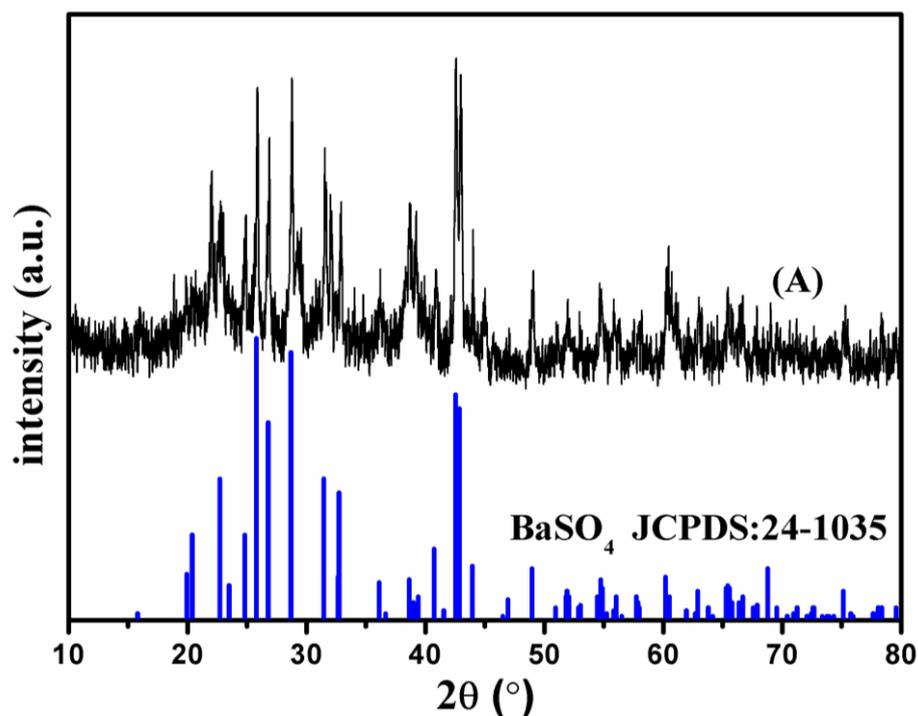


Figure S6. XRD patterns of the precipitates between oxidized products of thiophene and BaCl<sub>2</sub> (A) and the standard data of BaSO<sub>4</sub> (JCPDS card no. 24-1035).