

## Supporting Information

### **Insights into the sacrificial structure-activity relationship over a Ti-based metal-organic framework in oxidative desulfurization reaction**

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## 1. Materials

Tetrabutyl titanate ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ), Titanium tetrachloride ( $\text{TiCl}_4$ ), 1, 4-benzenedicarboxylic acid (BDC), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), benzothiophene (BT), N,N-dimethylformamide (DMF), acetic acid ( $\text{CH}_3\text{COOH}$ ), NaCl, methanol and *n*-octane were obtained from Shandong McLin Biochemical Technology Co., Ltd. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%), HF, HBr, NaF, NaBr, acetonitrile, tertiary butanol, ethanol, *p*-benzoquinone, and hydrochloric acid (HCl, 37%) were obtained from Sinopharm Chemical Reagent Co. All solvents and chemicals were analytically pure and used without further purification.

## 2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2550 diffractometer equipped with a SolX Detector-Cu K $\alpha$  radiation with wavelength of  $\lambda = 1.5418 \text{ \AA}$ . Scanning electron microscopy (SEM) images were recorded on SUPRA 55 operated with an acceleration voltage of 15 kV. Nitrogen sorption isotherms were obtained at 77 K on a BSD-PS1 gas sorption and porosimetry system (The samples were normally degassed at 423 K under vacuum until a final pressure of  $1 \times 10^{-3}$  Torr was reached prior to the measurement). Fourier transform infrared (FT-IR) spectra were recorded on a NicoLET iS10 spectrometer. Thermogravimetric analysis was carried out on TGA Q500. X-ray photoelectron spectroscopy (XPS) was performed on an Axis ultra DLD (Kratos analytical) with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). UV-visible diffuse reflectance spectra were recorded on a UV-2500 scanning spectrophotometer (Shimadzu). Ti content was determined with an iCAP 7600 ICP-OES analyzer calibrated with standard solutions.

## 3. Synthesis

Solvothermal preparation of MIL-125(Ti):  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  (0.52 ml, 1.5 mmol) and BDC (1 g, 6 mmol) were added into a mixture solution containing 18 ml DMF and 2 ml methanol under vigorous agitation at room temperature. After stirring 30 min, the mixture was transferred to a 40 ml Teflon-lined autoclave and placed in a pre-heated oven at 150 °C for 20 h. After cooling to room temperature, the resultant white solid

was washed twice with 10 mL DMF and with 50 mL ethanol at 70 °C for 6 h, respectively. Finally, the obtained sample was dried at 150 °C overnight.

Solvothermal preparation of Ti-BDC-A:  $\text{TiCl}_4$  (0.75 mmol, 83  $\mu\text{L}$ ) was taken by a pipette gun and immediately transferred into 15 mL of DMF solution at room temperature. Then, 5 mL of  $\text{CH}_3\text{COOH}$  was added. After stirring for 5 min, BDC (0.75 mmol, 0.125 g) was added into the above mixture until BDC was completely dissolved. After that, the obtained mixture was sealed in a 30 mL Teflonlined autoclave and placed in an oven at 150 °C for 24 h. After cooling, the resultant white solid was separately washed with 10 mL of DMF and then with 50 mL of ethanol at 70 °C for 6 h. Then, the sample was dried for 12 h at 150 °C.

#### 4. Catalytic tests

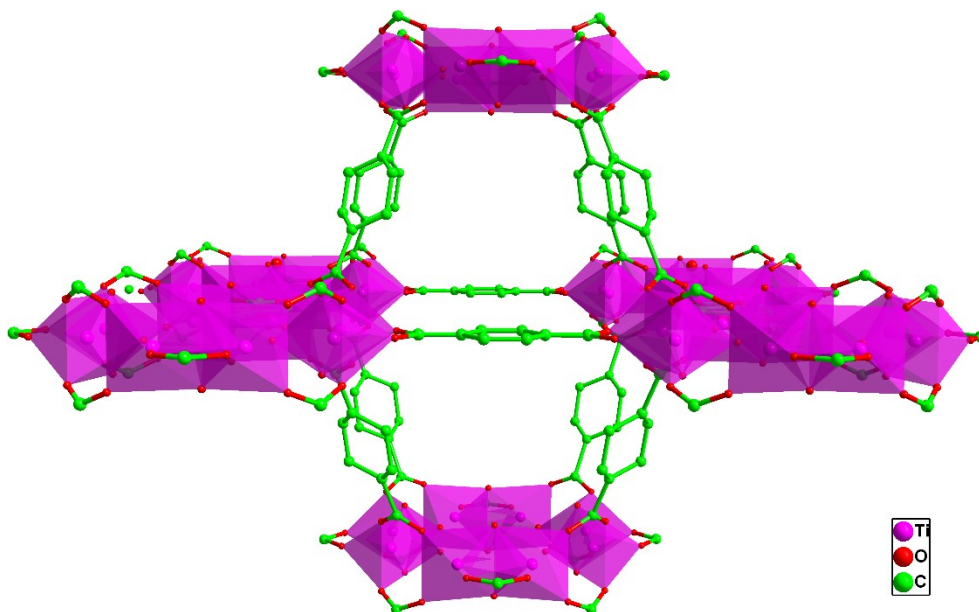
1000 ppm sulfur of DBT, 4,6-DMDBT or BT was dissolved in *n*-octane as model fuel oil, respectively. Model fuel oil (10 mL), acetonitrile as extractant (5 mL), Ti-MOF activated at 150 °C for 12 h as catalyst (30 mg), and 1 M HCl (50  $\mu\text{L}$ ) were orderly added into in a 30 mL dram vial. After that, the dram vial was immersed in 30 °C water bath with magnetic stirrer (800 rpm) for 8 min to obtain extraction balance. The reaction was initiated by adding  $\text{H}_2\text{O}_2$  as oxidant (30 wt.%) with a  $\text{H}_2\text{O}_2$ /sulfur (O/S) molar ratio of 5. The magnetic stirrer was stopped to make the reaction solution layered, after that the upper solution (model fuel oil) was withdrawn (all within 5 seconds), and analyzed by a Panna A60 gas chromatography (GC, FID detector with a 30 m packed HP5 column), and Agilent 7890B GC-MSD. The sulfur removal rate for the ODS reaction was calculated based on the follow equation:  $R = (1 - C_t/C_0) \times 100\%$  ( $C_t$  or  $C_0$  stands for the after-*t*-time reaction or initial concentration of sulfur).

The reusability of MIL-125(Ti) was performed at 30 °C in ODS of DBT. After each recycle, the MIL-125(Ti) was withdrawn by centrifugation without washing and reused in nest cycle with 50  $\mu\text{L}$  1 M HCl under the same ODS reaction condition.

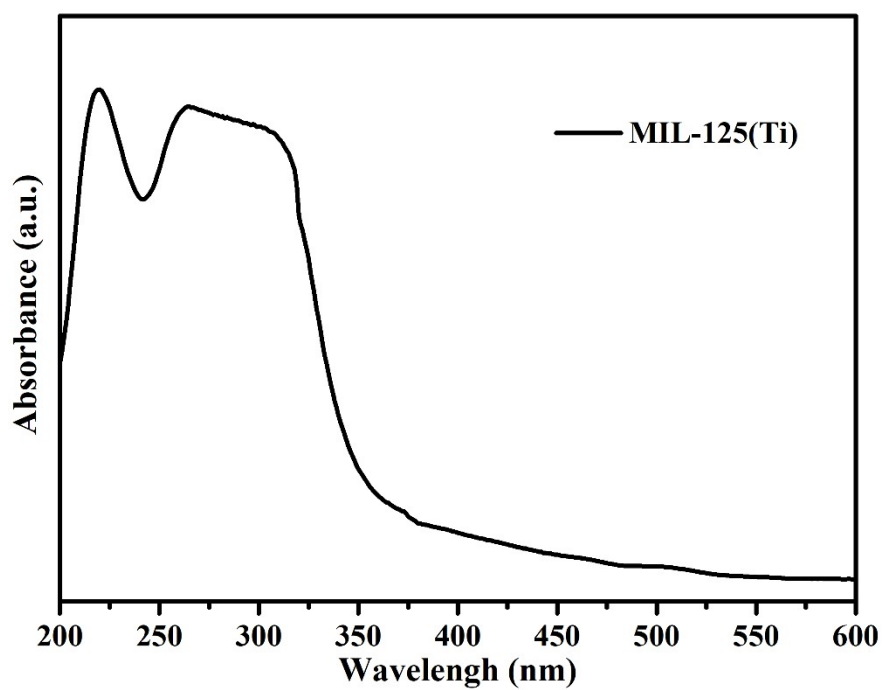
**Table S1** Ti content and N<sub>2</sub> sorption data of MIL-125(Ti).

Sample	Ti content (wt.%) <sup>a</sup>	BET surface area (m <sup>2</sup> /g)	Micropore volume (mL/g) <sup>b</sup>	Total pore volume (mL/g)
MIL- 125(Ti)	23.9	1712	0.77	0.98

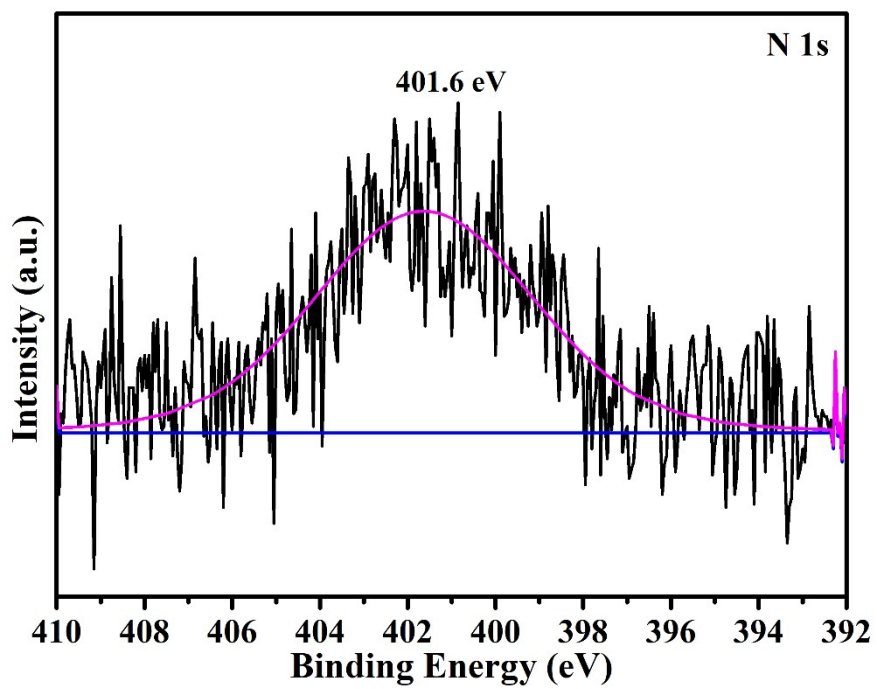
<sup>a</sup> Measured by ICP-OES, <sup>b</sup> Based on HK method.



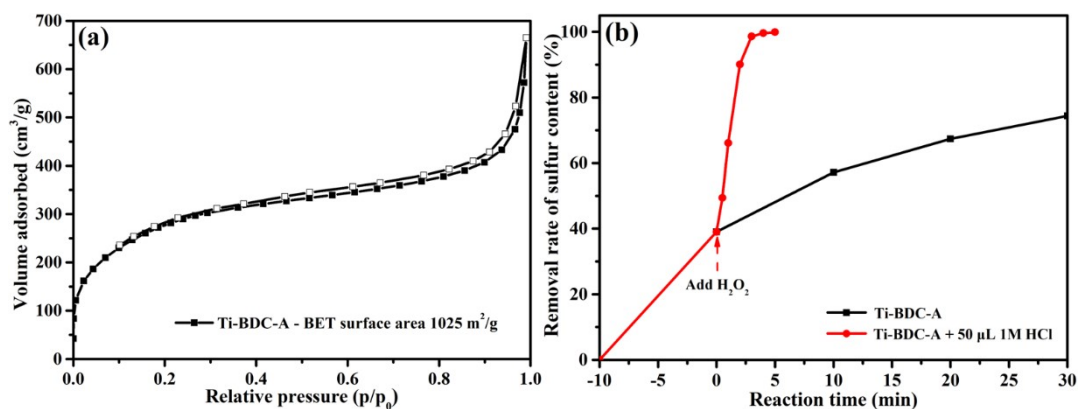
**Fig. S1** The structural diagram of MIL-125(Ti).



**Fig. S2** The UV-Vis spectrum of MIL-125(Ti).



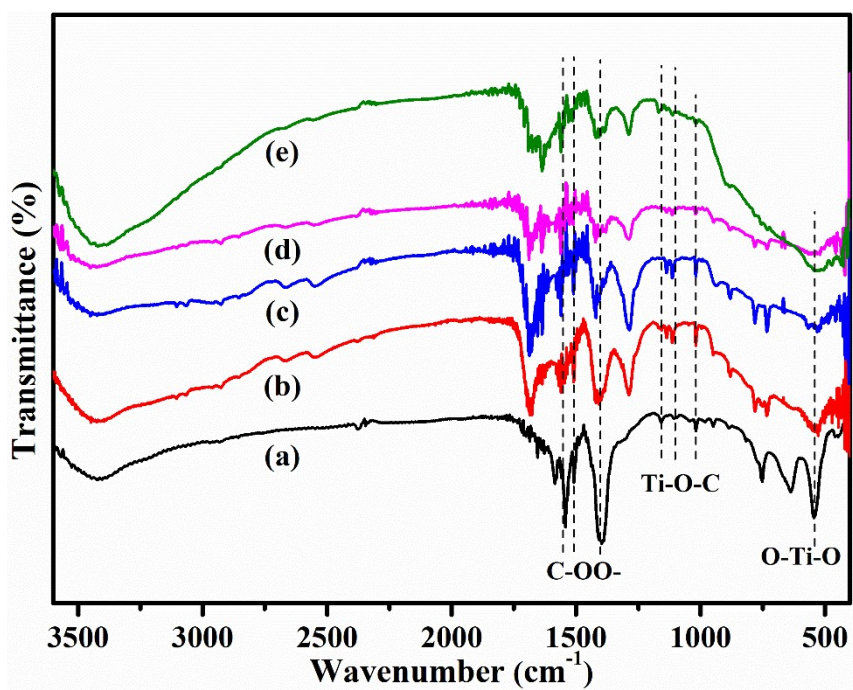
**Fig. S3** The XPS spectrum of MIL-125(Ti): N 1s.



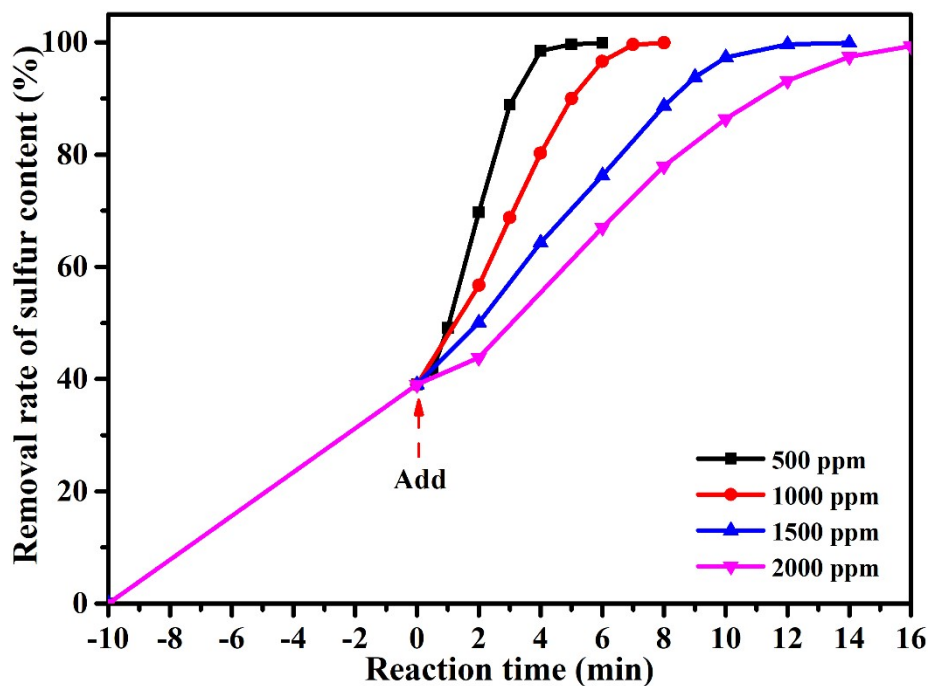
**Fig. S4** (a) The  $N_2$  sorption isotherm of Ti-BDC-A, (b) the ODS performance of Ti-BDC-A in the absence and presence of  $H^+$ . Reaction conditions: 30 mg catalyst, 10 mL oil, 5 mL acetonitrile, oxidant ( $H_2O_2$ , O/S molar ratio = 5), 1000 ppm sulfur, 30 °C.

Ti-BDC-A prepared via solvothermal method showed ordinary ODS activity, and 1000 ppm sulfur of DBT could be eliminated 86.7% at a reaction of 30 min. Notably, the ODS activity of Ti-BDC-A could be observably upgraded enhanced when 50  $\mu$ L 1M HCl was added into the same ODS system, and 1000 ppm sulfur of DBT could completely be eliminated at 5 min at 30 °C (Fig. S4).

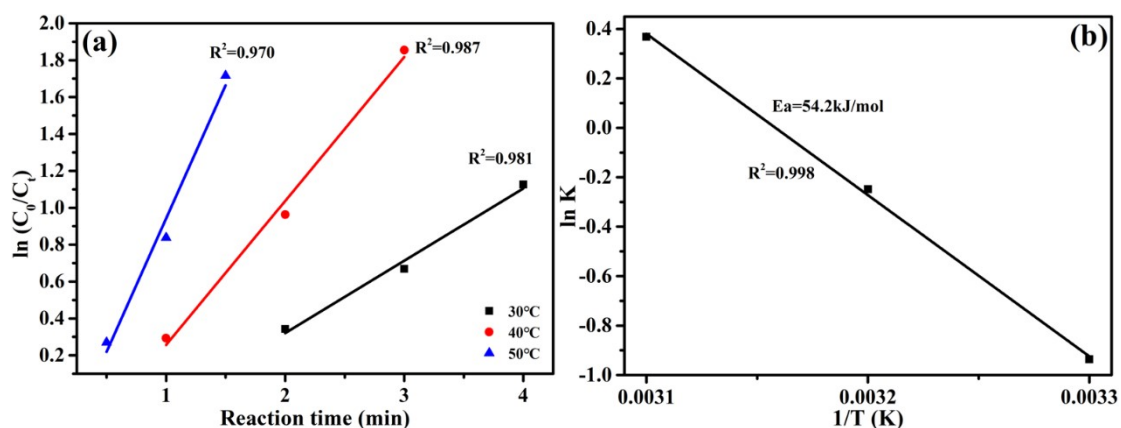




**Fig. S5** The FT-IR spectrum of (a) MIL-125(Ti)-fresh, (b) MIL-125(Ti)-reuse, (c) MIL-125(Ti) + HCl-reuse 1 time, (d) MIL-125(Ti) + HCl-reuse 5 times, (e) MIL-125(Ti) + HCl-reuse 10 times.



**Fig. S6** Influence of sulfur content on ODS performance of MIL-125(Ti) with the stimulation of 50  $\mu$ L 1 M HCl. Reaction conditions: 30 mg MIL-125(Ti), 10 mL oil, 5 mL acetonitrile, O/S molar ratio = 5 ( $\text{H}_2\text{O}_2$  as oxidant), 30  $^\circ\text{C}$ .

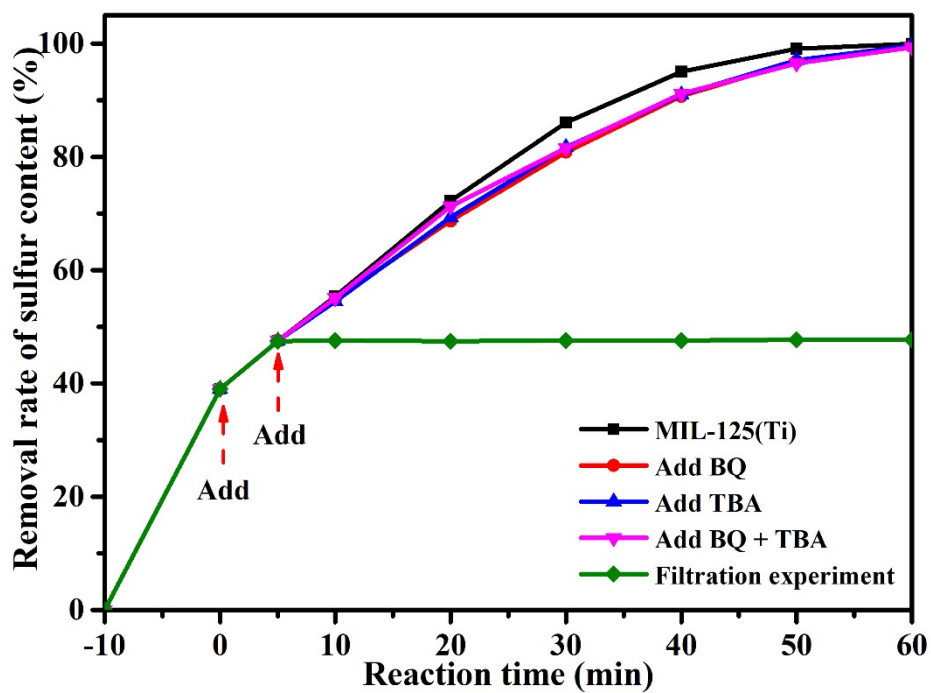


**Fig. S7** (a) Pseudo-first-order rate constants and (b) pseudo-first-order rate constants for DBT of ODS reaction at different temperatures over MIL-125(Ti) with the stimulation of proton.

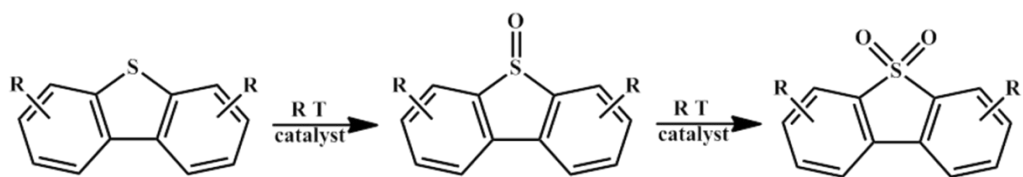
Based on the temperature-dependent catalyst performance, the  $k$  (reaction rate constants) and  $E_a$  (activation energy) were evaluated according to the first-order kinetic law:  $\ln(C_0/C_t) = -kt$  and  $\ln k = -E_a/RT$ , while  $C_0$  and  $C_t$  represent the sulfur content at the initial and  $t$  time (Figure S5). Based on the derived  $k$  values (Table S2), an  $E_a$  value of 54.2 kJ/mol was obtained.

**Table S2** Reaction rate constants were obtained at different temperatures in ODS of DBT.

Temperature (°C)	Reaction rate constant $k_{app}$ (min <sup>-1</sup> )	R <sup>2</sup>
30	0.3920	0.970
40	0.7805	0.987
50	1.4450	0.981



**Fig. S8** Leaching and quenching experiments over MIL-125(Ti) in the ODS reaction. Reaction conditions: MIL-125(Ti) (30 mg), model oil (10 mL), acetonitrile (5 mL) as extraction phase, 1000 ppm sulfur of DBT, oxidant ( $\text{H}_2\text{O}_2$ , O/S molar ratio = 5), 30 °C, *p*-benzoquinone (2.25 mmol) or tertiary butanol (4.5 mmol).



**Scheme S1** Reaction pathway about the ODS reaction of DBT or 4,6-DMDBT.