

Supplementary information

## **Oxidative desulfurization of dibenzothiophene with molecular oxygen using emulsion catalysis**

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Detailed Experiment Section

### Material

All chemical were commercial products used as supplied.  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  was prepared according to literature procedure (Tsigdinos G. A., Hallada C. J., Inorg. Chem. 1968, 7: 437)

### Synthesis of catalysts

$\text{Q}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  was prepared as follows: A solution of quaternary ammonium (5 mmol) in 20 ml ethanol was added dropwise into 40 ml aqueous solution of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (1 mmol) under stirring at room temperature. A brown precipitate was immediately formed. After continuously stirring for 2 h, the resulting mixture was filtered and dried at 60 °C in vacuum for 24 h to produce catalysts. There are three kinds of quaternary ammonium including  $[\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3]_5\text{Cl}$ ,  $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5\text{Cl}$ , and  $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_5\text{Cl}$ .

### Characterization of catalyst $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$

$^{31}\text{P}$  NMR and  $^1\text{H}$  NMR spectrums were recorded at 9.4 T on a Bruker DRX 400 spectrometer. The  $^{31}\text{P}$  MAS NMR spectra of the catalyst with high-power proton decoupling was performed at 161.9 MHz with a BBO MAS probe lead using 4 mm

ZrO<sub>2</sub> rotors and 2.0 μs pulse, and 2 s repetition time and 2048 scans, with the sample spun at 8 kHz. The <sup>31</sup>P chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> aqueous solution. The infrared spectrum of the catalyst, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 470 FT-IR spectrometer. Matrix-Assisted Laser Desorption/ Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF mass spectrometry) experiments were performed on a Bruker Autoflex time-of-flight mass spectrometer (Bruker, Bremen, Germany). This instrument was equipped with a delayed ion-extraction device and a pulsed nitrogen laser operated at 337 nm. The MALDI uses a ground-steel sample target with 384 spots. The range of laser energy was adjusted to slightly above the threshold to obtain good resolution and signal-to-noise ratio (S/N). The mass spectrum of catalyst reported was obtained in the positive ion linear mode with delayed extraction for 90 ns and calibrated using an external calibration equation generated from the ion signal of angiotension II and insulin chain B. And the mass spectrum was typically summed with 30 laser shots.

#### Oxidation of DBT present in acetonitrile

In this run, a water bath was heated to 60 °C. The DBT (147 mg, 0.8 mmol) was dissolved in a flask with 50 ml acetonitrile. The catalyst [C<sub>18</sub>H<sub>37</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (0.33 g, 0.01 mmol) and isobutyl aldehyde (0.72 ml, 8 mmol) were added to the solution simultaneously. Molecular oxygen was bubbled through the reaction solution. The mixture was stirred at 1000 rpm. The sample was periodically sampled and put into an ice chamber to stop the reaction. The process of

reaction was analyzed by a gas chromatography coupled with a flame photometric detector (GC-FPD) after the catalyst and sulfones were precipitated by centrifugation.

#### Oxidation of DBT present in decalin

In a typical run, a water bath was heated to 60 °C. The DBT (147 mg, 0.8 mmol) was dissolved in a flask with 50 ml decalin. The catalyst  $[C_{18}H_{37}N(CH_3)_3]_5PV_2Mo_{10}O_{40}$  (0.33 g, 0.01 mmol), acetonitrile and isobutyl aldehyde were added to the solution simultaneously. Molecular oxygen was bubbled through the reaction solution. The mixture was stirred at 1000 rpm and a turbid W/O emulsion was formed immediately.

The optical micrographs were obtained at decalin (50 ml), the catalyst (0.01 mmol), acetonitrile (50ml) and isobutyl aldehyde (0.72 ml, 8 mmol). The emulsion was periodically sampled and put into an ice chamber to stop the reaction. The process of reaction was analyzed by a gas chromatography coupled with a flame photometric detector (GC-FPD) after the catalyst and sulfones were precipitated by centrifugation. The sulfur content from DBT in decalin was determined by microcoulometry (detection limit: 0.1 ng/μl).

#### Analysis of sulfur content

According to the literature (Mure T, Craig F., Zbigniew R., App. Catal. A : Gen. 2001, 219 : 267.), DBT sulfone has very low solubility in decalin and it partly precipitated out during the reaction and subsequent sampling. The DBT content of the model diesel was determined by microcoulometry (detection limit: 0.1 ng/μl). The oxidation of DBT in acetonitrile was analyzed by a gas chromatography coupled with a flame

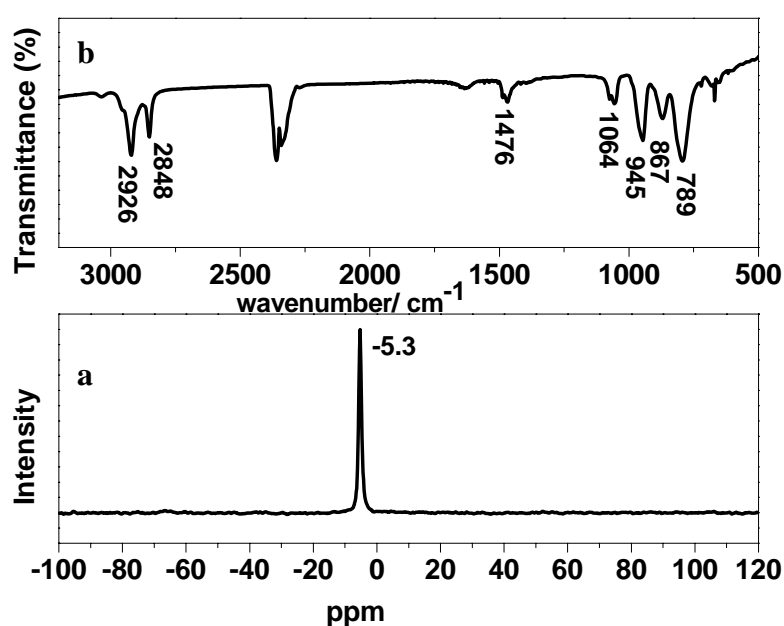
photometric detector (GC-FPD). Gas chromatography: Agilent 6890N equipped with a capillary column (PONA, 50 m × 0.2 mm, id × 0.5 μm); Flame photometric detector (FPD): Agilent H9261. Analysis conditions were as follows: injection port temperature, 280 °C; detector temperature, 250 °C; oven temperature program, 280 °C, hold for 8 min.; split ratio, 1/100; carrier gas, ultra-purity nitrogen; column flow, 0.9 ml/min; reagent gases, air flow of 100 ml/min, hydrogen flow of 75 ml/min; the injection volume of sample was 1 μl.

#### Some Results Section

**Figure S1.** Spectroscopic characterization of catalyst  $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ .

(a)  $^{31}\text{P}$  MAS NMR spectrum; (b) IR spectrum; (c)  $^1\text{H}$  NMR spectrum; (d)

MALDI-TOF mass spectrum.





C

1H NMR OF Lv HY in DMSO

ppm

3.3722  
3.3004  
3.2796  
3.2583  
3.0657  
2.5072  
1.6749  
1.2367  
0.8703  
0.8550  
0.8374  
0.0001

Integral

0.740  
3.148  
0.699  
10.771  
1.000

ppm 9 8 7 6 5 4 3 2 1

Current Data Parameters  
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EXPNO 184  
PROCNO 1

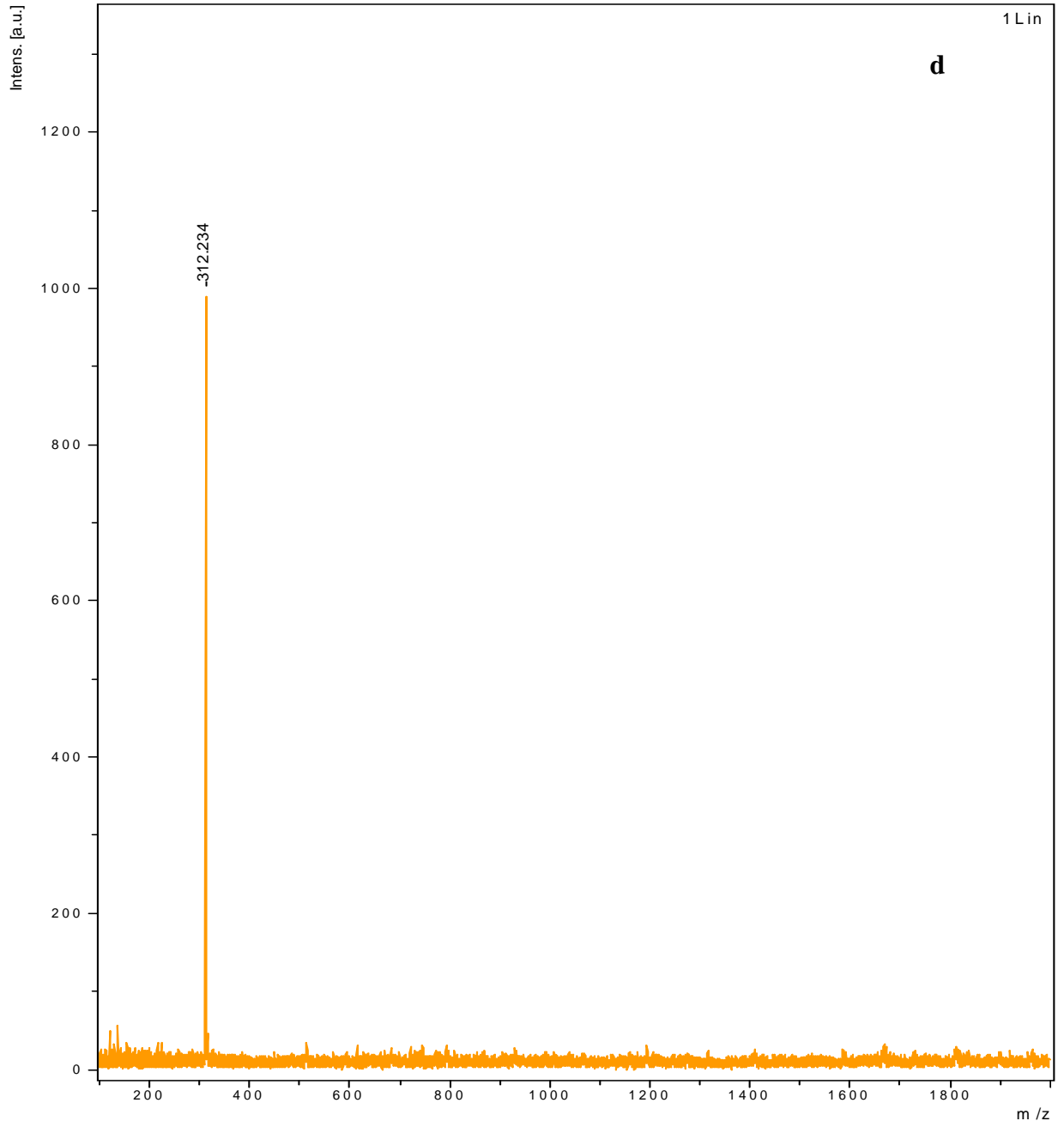
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NS 4  
DS 0  
SWH 6009.615 Hz  
FIDRES 0.183399 Hz  
AQ 2.7263477 sec  
RG 64  
DW 83.200 usec  
DE 6.00 usec  
TE 0.0 K  
D1 1.0000000 sec  
MCREST 0.0000000 sec  
MCWRK 0.0150000 sec

==== CHANNEL f1 =====  
NUC1 1H  
P1 8.20 usec  
PL1 5.00 dB  
SF01 400.1324753 MHz

F2 - Processing parameters  
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SF 400.1299991 MHz  
WDW GM  
SSB 0  
LB -0.50 Hz  
GB 0.1  
PC 1.40

1D NMR plot parameters  
CX 20.00 cm  
CY 30.00 cm  
F1P 10.000 ppm  
F1 4001.30 Hz  
F2P 0.000 ppm  
F2 0.00 Hz  
PPMCM 0.50000 ppm/cm  
HZCM 200.06500 Hz/cm





m/z	SN	Quality Fac.	Res.	Intens.	Area	
312.234	136.7	49092	999	989.00	374	

Table S1. Oxidation of DBT by molecular oxygen/ aldehyde in emulsion system

run	(CH <sub>3</sub> ) <sub>2</sub> HCHO (mmol)	CH <sub>3</sub> CN (ml)	Time (h)	Conversion of DBT <sup>a</sup> (%)
1	4	0	5	0
2	4	3	5	33
3	4	5	5	46
4	4	10	5	54
5	4	20	5	83
6	8	20	10	95
7	8	50	4	100

<sup>a</sup> Conversion of DBT was calculated as follows:  $\{1 - [(\text{DBT presence in decalin after reaction} + \text{DBT presence in MeCN}) / \text{DBT presence in decalin before reaction}]\}$   
conditions: [C<sub>18</sub>H<sub>37</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (0.33 g, 0.01 mmol), DBT (147 mg, 0.8 mmol) in 50 ml decalin, reaction temperature 60 °C and O<sub>2</sub> (1 atm)