Supporting Information for

Zr-based MOFs for oxidative desulfurization: What matters?

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Contents

1. Experimental section

1.1 Materials and instrumentation

Zirconium dichloride oxide octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99.9%), *p*-benzoquinone (>98%), 2,2,6,6-tetramethylpiperidinooxy (TEMPO, >98%) were purchased from Beantown Chemical. Zirconium (IV) chloride ($ZrCl_4$, 98%) was purchased from Alfa Aesar. Terephthalic acid (H_2BDC, >99%) was purchased from TCI. Biphenyl-4,4'-dicarboxylic acid (BPDC, >95%) was ordered from Oxchem. N,N-Dimethylformamide (DMF), methanol, *n*-tetradecane, acetonitrile and *n*-octane was purchased from EMD Millipore Corporation. Dibenzothiophene (DBT, 98%) was ordered from Sigma-Aldrich. 4,6-Dimethyldibenzothiophene (DMDBT, 98%) and hydrogen peroxide (H_2O_2, 30 wt%) was purchased from Thermo Fisher Scientific. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was ordered from Matrix Scientific. Dimethyl sulfoxide (DMSO) was purchased from Oakwood Chemical. All the chemicals were used as received without further purification.

TEM images of the HP-UiO-66 were obtained with a Philips TEM microscope at 200 kV. The samples were prepared by placing a drop of ethanol suspension of the sample onto a Formvar/Carbon film, 200 Mesh, Nickel and by allowing the solvent to evaporate. FTIR spectra were obtained on a Thermo Scientific Nicolet^{TM} iS^{TM} 10 spectrometer. X-ray diffraction (PXRD) patterns were collected on Rigaku Miniflex 600 using Cu Kα radiation. The ODS procedure, the oxidation products and the removal content of sulfur compounds were monitored and calculated through GC-MS analysis using a GCMS-QP2010 SE with DB-5 ms column from Shimadzu.

The X-band EPR spectra were recorded at room-temperature for liquid solutions using a Bruker EMX 6/1-HX spectrometer. This instrument was fitted with an ER041X microwave bridge, a high-sensitivity cylindrical resonator (ER4119HS-W1), and a Bruker AquaX cell. The experimental conditions are: microwave power 2.0 mW, microwave frequency 9.85 GHz, and modulation amplitude 1 G. The theoretical spectra were generated using the SpinCount program developed by Prof. Michael Hendrich at Carnegie Mellon University. The spectra were modeled considering a typical $S = 1/2$ spin-Hamiltonian which incorporated two ($I_1 = 1$, and $I_2 = 1/2$) nuclear spins.

1.2 Experimental procedures

Typical procedure for the synthesis of Zr-based MOFs

The MOFs were synthesized according to the reported procedures with some modification.[S1] Typically, for the synthesis of HP-UiO-66, $ZrOCl_2 \cdot 8H_2O$ (0.073 g, 0.227 mmol) and H_2BDC (0.034 g, 0.227 mmol) was dissolved in DMF (25 mL) at room temperature. The solution was then sealed in a 30 mL vial and maintained at 150 °C for 48 h. After cooling down to room temperature, the precipitate was recovered by centrifugation and soaked and washed with DMF. Then the solid was soaked and washed using methanol for several times before dried in vacuum oven.

For the synthesis of UiO-67, $ZrCl_4$ (0.067 g, 0.27 mmol) was dissolved in 5 mL DMF with 0.5 mL HCl. BPDC (0.09 g, 0.38 mmol) was dissolved in 10 mL DMF, followed by the addition of the $ZrCl_4$ solution. The solution was sealed in a 30 mL vial and sonicated for 20 mins. The vial was put into an oven of 80 °C for 15 h. After cooling down to room temperature, the precipitate was recovered by centrifugation and soaked and washed with DMF. Then the solid was soaked and washed using methanol for several times before dried in vacuum oven.

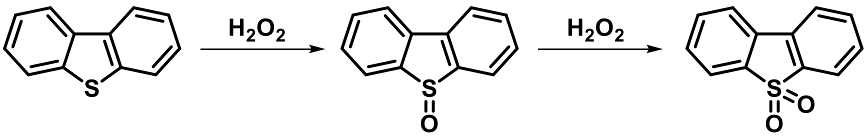
Typical procedure for ODS process

The ODS reaction was carried out using a two-phase extraction-oxidation procedure. In a typical reaction, 30 mg HP-UiO-66 was dispersed in 10 g acetonitrile in a 100 mL round bottom flask. To the dispersion, 10 g model oil (1000 ppmw S from DBT in *n*-octane) was added. The flask was heated in an oil bath at desired temperatures and stirred for 10 min to reach the equilibrium of extraction. At this point, appropriate amounts of H_2O_2 solution was added to start the oxidation reaction. During the reaction, a small aliquot of the oil phase was taken at different times and analyzed by GC-MS using *n*-tetradecane as internal standard to calculate the removal content of DBT.

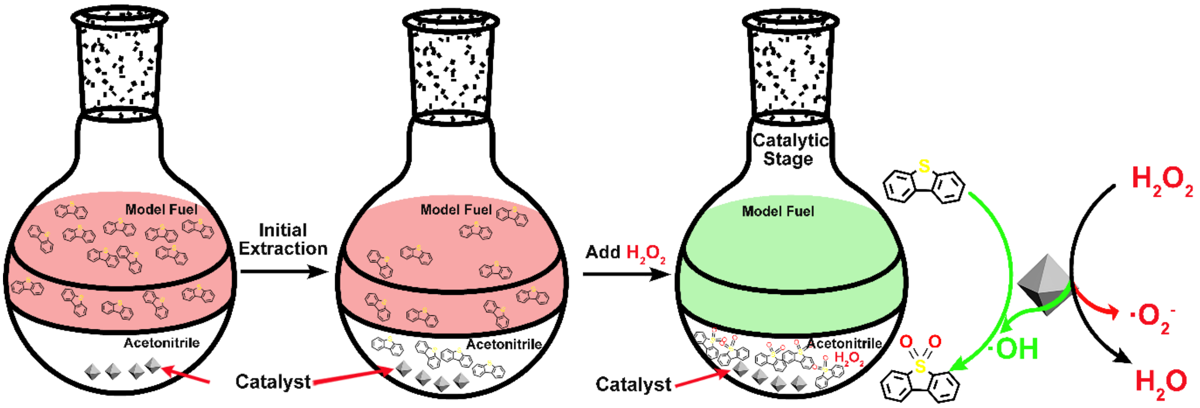
The reaction procedure for DMDBT was very similar to that of DBT, except for that model oil with DMDBT (1000 ppmw S from DMDBT in *n*-octane) was used. For the recycling experiments, HP-UiO-66 was collected and washed with acetonitrile after each reaction to remove the adsorbed substances for next cycle.

For the control reactions, 30 mg HP-UiO-66 was dispersed in 10 g model oil with DBT and 4 equivalents of hydrogen peroxide. In different control reactions, TEMPO, or DMSO, or *p*-benzoquinone was added to the reaction solution, respectively. The reaction solution was stirred at 30 °C for 60 minutes. After reaction, GC-MS was used to detect the products and calculate the removal content of DBT.

2. The oxidation reaction of DBT



Scheme S1 The oxidation of DBT to its corresponding sulfoxide and sulfone



Scheme S2 Schematic illustration of the ODS process with a two phase reaction system catalyzed by HP-UiO-66 and possible mechanism of the reaction

3. TEM images of the HP-UiO-66

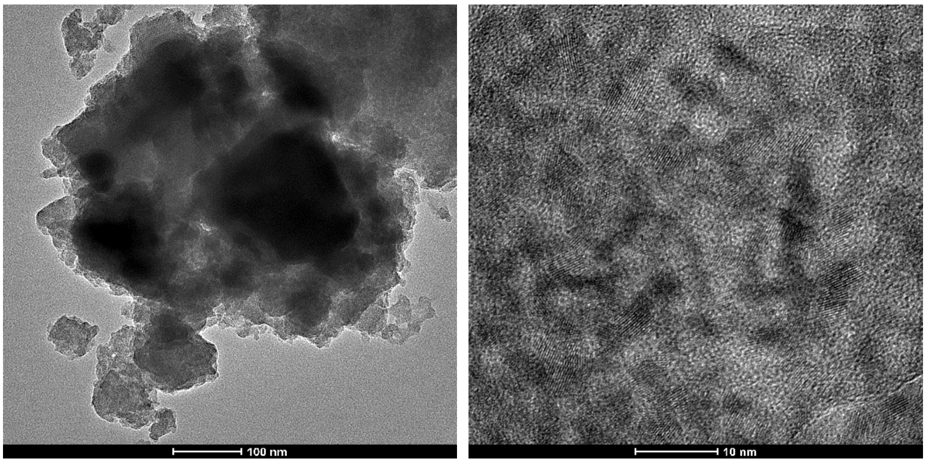


Figure S1 TEM images of the HP-UiO-66

4. The extraction of DBT from oil to acetonitrile with time

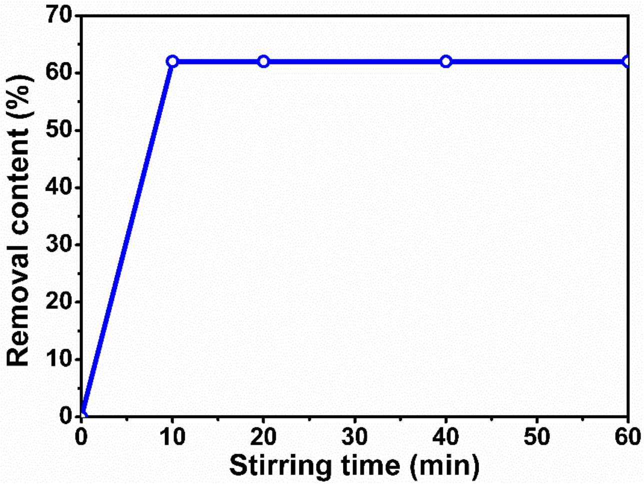


Figure S2 Extraction equilibrium of DBT from oil phase to acetonitrile phase

5. The effect of temperature on ODS of DBT

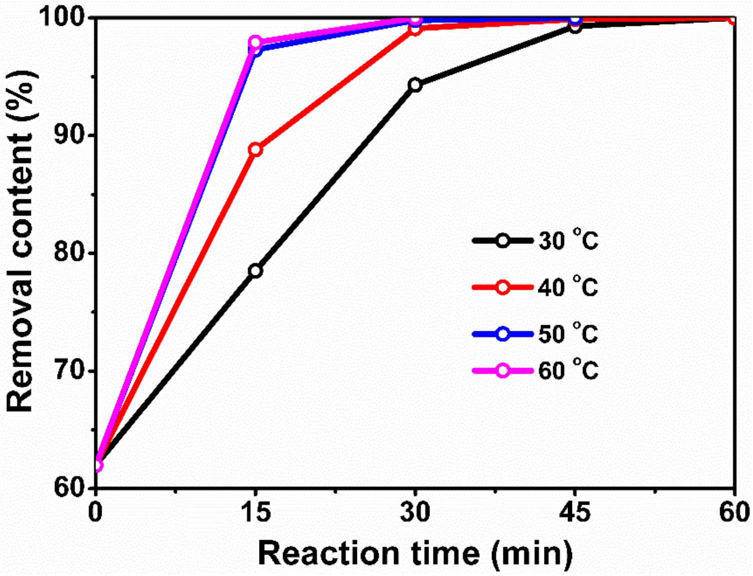


Figure S3 ODS reaction of DBT at different temperatures. Reaction conditions: HP-UiO-66 (30 mg); 1000 ppmw DBT in n-octane (10 g); acetonitrile (10 g); H_2O_2 (4 equivalents to the amount of DBT)

6. The effect of oxidant amount on ODS of DBT

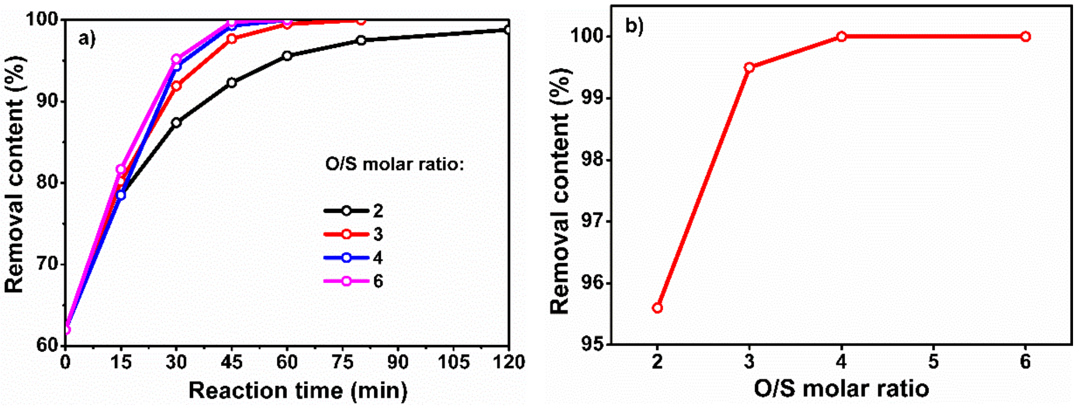


Figure S4 a) ODS reaction of DBT with different amount of oxidant. b) Removal content of DBT with different amount of oxidant. Reaction conditions: HP-UiO-66 (30 mg); 1000 ppmw DBT in n-octane (10 g); acetonitrile (10 g); 30 °C

7. The effect of catalyst amount on ODS of DBT

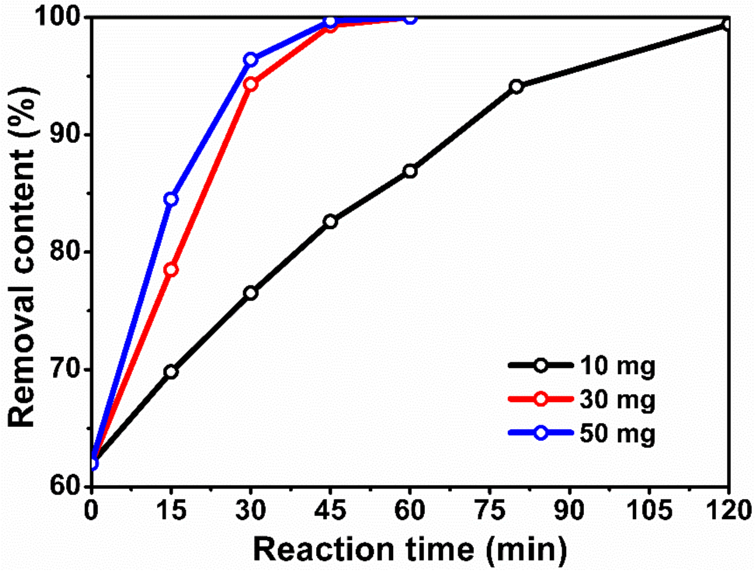


Figure S5 ODS reaction of DBT with different amount of HP-UiO-66. Reaction conditions: 1000 ppmw DBT in n-octane (10 g); acetonitrile (10 g); H_2O_2 (4 equivalents to the amount of DBT); 30 °C

8. N_2 adsorption-desorption analysis of HP-UiO-66 after reuse

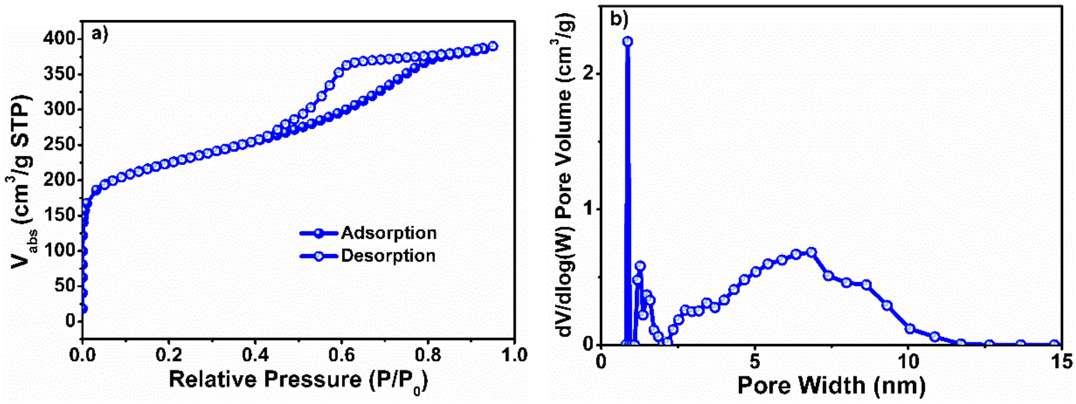


Figure S6 a) N_2 sorption isotherm of HP-UiO-66 after reuse in ODS reaction of DBT. b) Pore size distribution of the reused HP-UiO-66. N_2 adsorption data were collected on a Micrometrics ASAP 2020 Plus accelerated surface area and porosimetry system at 77 K surface area and pore size analyzer. Samples were activated under vacuum at 150 °C for 12 h with the activation port equipped on ASAP 2020.

9. PXRD pattern of the HP-UiO-66 before and after reaction

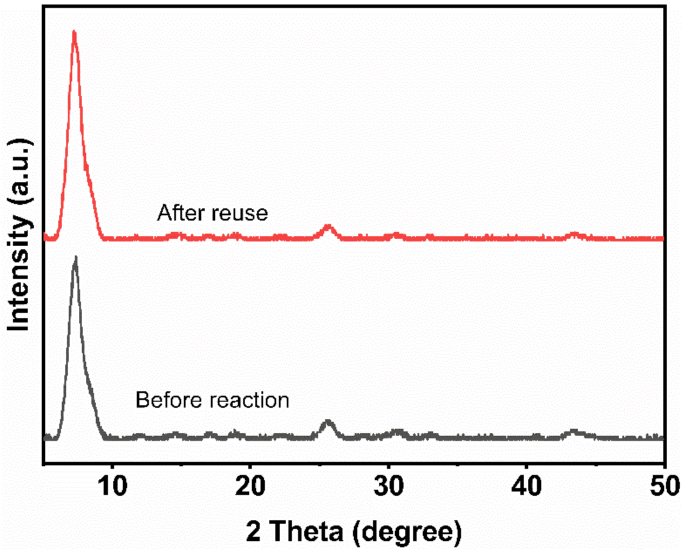


Figure S7 PXRD pattern of HP-UiO-66 before reaction and after reuse in ODS reaction of DBT

10. FT-IR spectra of the HP-UiO-66 before and after reaction

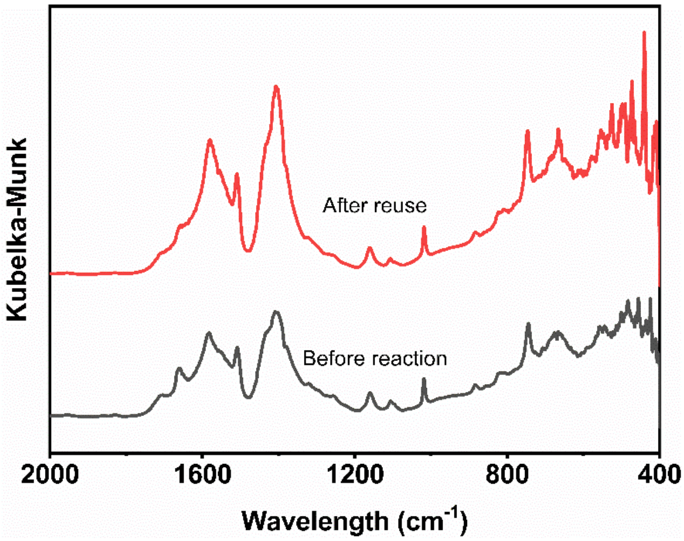


Figure S8 FT-IR spectra of HP-UiO-66 before reaction and after reuse in ODS reaction of DBT

11. TEM image of the HP-UiO-66 after reuse

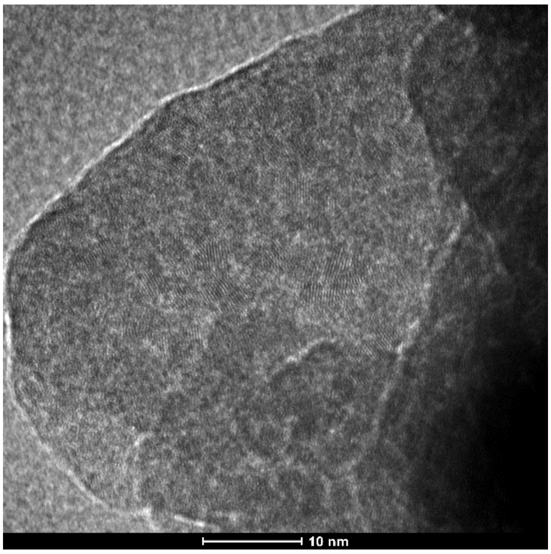


Figure S9 TEM image of HP-UiO-66 after reuse in ODS reaction of DBT

12. ODS performance of DMDBT with different Zr-based MOFs

Table S1 Comparison of Zr-based MOFs on ODS performance of DMDBT

Entry	Catalyst/amount	DMDBT concentration/amount	O/S molar ratio	T/°C	t/min	Removal content/%	Ref.
1	HP-UiO-66/30 mg	1000 ppmw/10 g	4	30	80	100	-
2	UiO-66-free/50 mg	500 ppmw/10 g	6	60	120	98.1	[S2]
3	NU-1000/40 mg	500 ppmw/10 g	6	60	120	61.6	[S3]
4	UiO-66/100 mg	500 ppmw/10 mL	12	60	180	72.5%	[S4]
5	MOF-808/15.5 mg	1000 ppmw/2 mL	5	40	5	94.7	[S5]

13. Performance of HP-UiO-66 in ODS of model oil with high content of DBT

Table S2 Performance of HP-UiO-66 for ODS of high sulfur content model oil

t/min Removal content/% S content	60	90	120	150	180	210	240
2000 ppmw	93.0	99.7	100				
3000 ppmw	77.1	--	90.1	95.0	98.6	99.9	100

Reaction conditions: DBT in *n*-octane (10 g); acetonitrile (10 g); HP-UiO-66 (30 mg); H_2O_2/S molar ratio=4; 30 °C.

14. References

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