Supporting Information for

Zr-based MOFs for oxidative desulfurization: What matters?

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1. Experimental section

1.1 Materials and instrumentation

Zirconium dichloride oxide octahydrate (ZrOCl₂·8H₂O, 99.9%), p-benzoquinone (>98%), 2,2,6,6-tetramethylpiperidinoxy (TEMPO, >98%) were purchased from Beantown Chemical. Zirconium (IV) chloride (ZrCl₄, 98%) was purchased from Alfa Aesar. Terephthalic acid (H₂BDC, >99%) was purchased from TCI. 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 (H₂O₂, 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™ iS™ 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 (I₁ = 1, and I₂ = 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.[5] Typically, for the synthesis of HP-UiO-66, ZrOCl₂·8H₂O (0.073 g, 0.227 mmol) and H₂BDC (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, ZrCl₄ (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 ZrCl₄ 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$_2$O$_2$ 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](image)

Scheme S1 The oxidation of DBT to its corresponding sulfoxide and sulfone
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$_2$O$_2$ (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); H₂O₂ (4 equivalents to the amount of DBT); 30 °C

8. N₂ adsorption-desorption analysis of HP-Uio-66 after reuse

Figure S6 a) N₂ sorption isotherm of HP-Uio-66 after reuse in ODS reaction of DBT. b) Pore size distribution of the reused HP-Uio-66. N₂ 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

![PXRD pattern of HP-UiO-66](image)

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

![FT-IR spectra of HP-UiO-66](image)

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst/amount</th>
<th>DMDBT concentration/amount</th>
<th>O/S molar ratio</th>
<th>T/°C</th>
<th>t/min</th>
<th>Removal content/%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HP-Uio-66/30 mg</td>
<td>1000 ppmw/10 g</td>
<td></td>
<td>4</td>
<td>30</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>UiO-66-free/50 mg</td>
<td>500 ppmw/10 g</td>
<td></td>
<td>6</td>
<td>60</td>
<td>120</td>
<td>98.1</td>
</tr>
<tr>
<td>3</td>
<td>NU-1000/40 mg</td>
<td>500 ppmw/10 g</td>
<td></td>
<td>6</td>
<td>60</td>
<td>120</td>
<td>61.6</td>
</tr>
<tr>
<td>4</td>
<td>UiO-66/100 mg</td>
<td>500 ppmw/10 mL</td>
<td>12</td>
<td>60</td>
<td>180</td>
<td></td>
<td>72.5%</td>
</tr>
<tr>
<td>5</td>
<td>MOF-808/15.5 mg</td>
<td>1000 ppmw/2 mL</td>
<td>5</td>
<td>40</td>
<td>5</td>
<td></td>
<td>94.7</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>S content ppmw</th>
<th>t/min</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
<th>210</th>
<th>240</th>
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<tr>
<td>2000 ppmw</td>
<td></td>
<td>93.0</td>
<td>99.7</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3000 ppmw</td>
<td></td>
<td>77.1</td>
<td>--</td>
<td>90.1</td>
<td>95.0</td>
<td>98.6</td>
<td>99.9</td>
<td>100</td>
</tr>
</tbody>
</table>

Reaction conditions: DBT in n-octane (10 g); acetonitrile (10 g); HP-Uio-66 (30 mg); H2O2/S molar ratio=4; 30 °C.
14. References


