## Electronic Supplementary Information (ESI) for

# Design of a cage-core-chain structure catalyst for deep catalytic oxidative desulfurization with enhanced substrate enrichment

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#### Experimental

### Materials

Glacial acetic acid (99.8%, GC grade), n-octane (AR grade, 96%), N,N-dimethylformamide (AR grade, 99.5%), terephthalic acid (AR grade, 99%), FeCl<sub>3</sub>·6H<sub>2</sub>O (AR grade, 99%), phosphotungstic acid hydrate (H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub>·xH<sub>2</sub>O, AR grade), ethyl acetate (AR grade, 99.7%), 1-chlorobutane (98%), N-methylimidazole (99%), absolute ethanol (AR grade, 99.8%), 5,5dimethyl-1-pyrroline N-oxide (DMPO, 97%), 1,4-benzoquinone (*p*-BQ, AR grade, 99%), isopropanol (IPA, ACS grade, 99.5%), thiophene (T, AR grade, 99%), benzothiophene (BT, AR grade, 97%), dibenzothiophene (DBT, AR grade, 98%), were purchased from Shanghai McLean Biochemical Technology Co., Ltd. L-histidine (99%), 4-amino-2,2,6,6tetramethylpiperidine (TEMP, GC grade, >98%), 2-methylbenzothiophene (2-MBT, AR grade, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, AR grade, 97%) were purchased from Shanghai Aladdin Reagent Co. Ltd. Hydrogen peroxide (30%, AR grade) was obtained from Tianjin Oubo Kai Chemical Products Sales Co. Ltd. None of the chemicals were further purified before the experiment.

#### Characterization

Fourier transform infrared spectroscopy spectra (FT-IR) spectra were analyzed on Thermo Fisher (KBr pellets, Nicolet 6700, American). X-ray diffraction (XRD) patterns were obtained using a d/max-2500 X-ray diffractometer. The surface morphology and crystal structure of materials were characterized using a scanning electron microscope (SEM, Zeiss Merlin Compact, German). The N<sub>2</sub> physical adsorption-desorption isotherms of materials were obtained using Autosorb-iQ fully-automated surface area and porosity analyzer (Quantachrome Instruments, American). The thermal stability of materials was evaluated using thermal gravimetric analysis (TGA, NETZSCH TG 209F3 instrument). The elemental analysis of composite materials was obtained from the scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS: SEM, Zeiss Merlin Compact, Germany; EDS, Oxford x-max, U.K., Spray gold: pure platinum). The variations in surface electron state, electronic structure, chemical binding, and valance band position, of the as-prepared samples, were characterized by means of X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alphawith, Al Kα radiation at 15 kV). The ROSs generated during the sulfide oxidation reaction process were detected using a German Bruker A300 Electron Paramagnetic Resonance (EPR) spectrometer. The concentration of  $H_2O_2$  was measured with a concentration meter (PAL-39S, ATAGO, Japan). Contact angle measurement: Take an appropriate amount of finely ground powder sample and place it in the infrared pressing mold. Press it into a molded sheet using an infrared press. Then place it on the JY-82 contact angle testing platform, and determine the contact angle using the goniometry method. The in-situ Raman spectroscopy tests were conducted using a Raman spectrometer (Horiba LabRAM HR Evolution, Japan) with a 785 nm laser, a grating scale of 600 gr/mm, a hole size of 400  $\mu$ m, and an exposure time of 30 s/60 s. Analysis of the sulfur species in the samples was done using an SP-3420A gas chromatograph (GC) (Beijing Beifen Ruili Analytical Instrument Co. Ltd) with a flame photometric detector (FPD). The sulfur content of both the model oil and the actual diesel was measured using a THA-2000S UV fluorescence sulfur analyzer (Taizhou Jinhang Analytical Instrument Co. Ltd).



Fig. S1. (a) Simulation diagram assuming that HPW is encapsulated in a MIL-100(Fe) cage. (b) Fragmented structure of HPW@MIL-100(Fe) after DFT optimization.



Fig. S2. The size of [Bmim]Cl calculated by DFT.



Fig. S3. BET surface area and pore size distribution of HPW@MIL-101(Fe) with different amounts of HPW. (a) 3 g HPW, (b) 4 g HPW, (c) 5 g HPW, (d) 6 g HPW, (e) 7 g HPW

HPW@MIL-101(Fe) with	DBT removal rate	DBT removal rate	DBT removal rate
different amounts of HPW	(reacting 20 min)	(reacting 40 min)	(reacting 60 min)
3 g-HPW@MIL-101(Fe)	32.83%	44.06%	52.57%
4 g-HPW@MIL-101(Fe)	49.08%	62.87%	72.33%
5 g-HPW@MIL-101(Fe)	52.61%	61.24%	75.87%
6 g-HPW@MIL-101(Fe)	50.95%	61.36%	76.42%
7 g-HPW@MIL-101(Fe)	50.10%	60.89%	73.84%

Table. S1. DBT removal efficiency of HPW@MIL-101(Fe) with different amounts of HPW

Reaction conditions: V (DBT model oil) =10 mL, V(AcOH) =2 mL, V(H<sub>2</sub>O<sub>2</sub>)=0.3 mL, m(catalyst)= 0.04 g,

t=60 min, T = 60 °C.





Engegy(Ke V)) Fig. S4. (a) EDS of (a) 3 g-HPW@MIL-101(Fe). (b) 4 g-HPW@MIL-101(Fe) (c) 5 g-HPW@MIL-101(Fe), (d) 6 g-HPW@MIL-101(Fe)





Fig. S5. (a) EDS mapping image of 3 g-HPW@MIL-101(Fe). (b) EDS mapping image of 4 g-HPW@MIL-101(Fe) (c) EDS mapping image of 5 g-HPW@MIL-101(Fe), (d) EDS mapping image of 6 g-HPW@MIL-101(Fe)

Table. S2. The concentration of  $\mathrm{H}_{2}\mathrm{O}_{2}$  under the reaction conditions

Reaction time (min)	0 min	10 min	30 min	60 min	90 min
Concentration of $H_2O_2$ (g/100g)	4.0	3.9	3.7	3.7	3.6

Reaction conditions: V(H<sub>2</sub>O<sub>2</sub>)=0.3 mL, T = 60 °C.



Video S1: Dynamic contact angle of n-octane and [Bmim]PW@MIL-101(Fe). Contact angle measurement: Take an appropriate amount of finely ground powder sample and place it in the infrared pressing mold. Press it into a molded sheet using an infrared press. Then place it on the JY-82 contact angle testing platform. Utilize the equipment's automatic titration system to drop the testing reagent, capture testing photos, and determine the contact angle using the goniometry method.



Fig. S6. In-situ Raman spectra of HPW, MIL-101(Fe), and [Bmim]PW@MIL-101(Fe) in the H<sub>2</sub>O<sub>2</sub>-AcOH reaction system. The in-situ Raman spectroscopy tests were conducted using a Raman spectrometer (Horiba LabRAM HR Evolution, Japan) with a 785 nm laser, a grating scale of 600 gr/mm, a hole size of 400 μm, and an exposure time of 30 s. The testing process was carried out at 60 °C, with a reaction system consisting of 2 mL acetic acid, 0.3 mL hydrogen peroxide, and 40 mg of catalyst sample. Each sample was measured at three different positions, with three measurements taken at each position and averaged to obtain the final spectral data for that point. A total of nine measurements were performed per sample, with a total testing time of 18 mins per sample. Once the instrument parameters were set, it automatically conducted three measurements, and the average was taken as the final test result.



Fig. S7. Differential charge density of HPW@MIL-101(Fe) (blue and yellow regions represent charge depletion and accumulation, respectively).

Explanation: To further elucidate the interaction and electron transfer between HPW and MIL-101(Fe), DFT calculations were conducted to analyze the HPW@MIL-101(Fe) composite. A 3D charge density difference was performed to visually depict the electron transfer and redistribution. As shown in Fig. S4, charge accumulation is depicted in yellow, while charge depletion is shown in blue. The variation in interfacial charge density indicates that electrons are transferred from MIL-101(Fe) to HPW through the Fe-O-W bridging bond, resulting in electron depletion on MIL-101(Fe) and accumulation primarily on the HPW connected to MIL-101(Fe) (particularly in the W-O bond and W atom regions). This reveals that the W-O bonds and W atoms in HPW act as the primary electron acceptors. These findings are consistent with the results from XPS analysis.



Fig. S8. (a) Simulated diagram of hypothetical  $H_2O_2$  adsorption and dissociation into \*OOH on [Bmim]PW@MIL-101(Fe). (b) Optimized adsorption results of  $H_2O_2$  on the catalyst after DFT calculations.



Fig. S9. Time-Resolved in-situ Raman spectra of [Bmim]PW@MIL-101(Fe) in the H<sub>2</sub>O<sub>2</sub>-AcOH reaction system. The in-situ Raman spectroscopy tests were conducted using a Raman spectrometer (Horiba LabRAM HR Evolution, Japan) with a 785 nm laser, a grating scale of 600 gr/mm, a hole size of 400  $\mu$ m, and an exposure time of 60 s. The testing process was carried out at 60 °C, with a reaction system consisting of 2 mL acetic acid, 0.3 mL hydrogen peroxide, and 40 mg of catalyst sample. The sample was measured at seven time points, with three measurements taken at each time point and averaged to obtain the final spectral data for that point. The total testing time for the sample was 60 min. Once the instrument parameters were set, it automatically conducted three measurements, and the average was taken as the final test result.

The experimental procedures for adsorptive desulfurization and extraction of DBT from composite material [Bmim]PW@MIL-101(Fe) are as follows: Firstly, 0.04 g of composite material was added into 10 mL of DBT model oil (1000 ppm) at 60 °C, and the mixture was stirred for 60 min. Then, the utilized composite material was separated from the mixture by centrifuging it. The separated composite material is then introduced into 10 mL of octane to extract the adsorbed DBT. Thereafter, centrifugation was used again to separate the octane solution and the composite material. The octane solution after extraction of DBT was analyzed by a GC. A DBT peak was detected in this solution, and the result has been plotted in Fig. S8. The experimental results demonstrate that the composite material adsorbed DBT from the model oil, and the DBT adsorbed was extracted by fresh octane, hence offering convincing proof of the composite material's capacity for DBT adsorption.



Fig. S10. Gas Chromatography analysis of DBT in octane solution.



Fig. S11. FI-IR of [Bmim]PW@MIL-101(Fe) composite material before and after oxidation desulfurization.

Catalysts	Model oil	Reaction conditions	Total	Refere
		Reaction conditions	desulfurization/%	nces
PTA@MIL-101(Cr)	BT	45 °C, 180 min, O/S=50, m(catalyst) = 0.075 g, 10 mL model oil (2684 ppm), CTAB=30mg	91	1
HPW(x)/MI-100(Fe)	DBT	50 °C, 90 min, O/S=4, m(catalyst) = 0.06 g, 2.5 mL model oil (500 ppm)	100	2
BMImPW@MIL- 101(Cr)	BT	50 °C, 120 min, O/S=8, m(catalyst) = 0.06 g, 20 mL model oil (500 ppm)	100	3
PW11Zn@MOF-808	DBT	50 °C, 30 min, O/S=5, m(catalyst) = 0.03 g, 10 mL model oil (500 ppm)	99.4	4
CoWPOM@MIL- 101(Cr)	DBT	55 °C, O/S=15, m(catalyst) = 0.1 g, 5 mL model oil (500 ppm), CTAB (certain amount)	98.1	5
PW4@UIO-66-NH2/GO	model diesel	70 °C, 60 min, O/S=8.4, catalyst (certain amount), 0.75 mL model oil, [Bmim]PF <sub>6</sub> =0.75 mL	99.9	6
LaW <sub>10</sub> O <sub>36</sub> @MIL- 101(Cr),	DBT	60 °C, 120 min, O/S=6, m(catalyst) = 0.04 g, 5 mL model oil	99.1	7
PMA/UiO-66	DBT	80 °C, 120 min, O/S=3, m(catalyst) = 0.05 g, 10 mL model oil (500 ppm)	100	8
PMoV <sub>1/2/3</sub> @rht-MOF-1	DBT	70 °C, 50 min, O/S=12, m(catalyst) = 0.06 g, 5 mL model oil (1000 ppm)	96	9
[Bmim]PW@MIL- 101(Fe)	DBT	60 °C, 60 min, O/S=13, m(catalyst) = 0.04 g, 10 mL model oil (1000 ppm)	99.03	This work

Table S3. Comparison of the catalytic activity with some other catalysts

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