

## Supporting Information

### **Fabrication of $\text{IMo}_6\text{iPAF-1}$ as enzyme mimics in heterogeneous catalysis for oxidative desulfurization under $\text{O}_2$ or air**

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## Supplementary captions

## Materials and Methods

**Fig. S1** SEM and EDAX elemental analyses of  $\text{IMo}_6@\text{iPAF-1}$ .

**Fig. S2** The EDS mapping of iPAF-1 loaded with  $\text{IMo}_6$ . (Color code: Brownish red: Na; Pink: Mo; Yellow: I; Blue: C; Green: N; and Red: O).

**Fig. S3** The XPS spectra of Mo3d of  $\text{IMo}_6$  and  $\text{IMo}_6@\text{iPAF-1}$  (a), O1s of  $\text{IMo}_6$  and  $\text{IMo}_6@\text{iPAF-1}$  (b).

**Fig. S4** Photo image of white needle crystals deposited from the decalin with the catalyst  $\text{IMo}_6@\text{iPAF-1}$ .

**Fig. S5** FT-IR spectra of  $\text{IMo}_6@\text{iPAF-1}$  before reaction and after reaction (a), post-reaction solution (b).

**Fig. S6** GC-FID chromatogram for the oxidation of cyclohexene and toluene. The left curve shows the chromatogram before oxidation; The right curve shows the chromatogram after oxidation. Reaction conditions: 10 mg of catalyst, oxidant  $\text{O}_2$ , 90 °C for 5 h.

**Fig. S7** Aerobic oxidation of  $\text{S}^{2-}$  in the presence of  $\text{IMo}_6@\text{iPAF-1}$  under their reaction conditions as:  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (0.1mmol, 10 mL  $\text{H}_2\text{O}$ ), catalyst (10 mg) at 80 °C with  $\text{O}_2$ .

**Fig. S8** Main parameters on DBT conversion: (a) Different reaction temperatures (b) Concentration of substrate and (c) Usage of catalysts.

**Fig. S9** GC-MS spectrum of the reaction product (dibenzothiophene sulfone).

**Fig. S10** DBT in the presence of different catalysts (10 mg) at 120 °C with air for 24 h.

**Fig. S11** Photo image of white needle crystals deposited from the decalin with the catalyst (a) $\text{IMo}_6$  (b) $\text{IMo}_6@\text{iPAF-1}$ .

**Fig. S12** UV-Vis spectrum of  $\text{IMo}_6@\text{iPAF-1}$  dissolved in decalin.

**Fig. S13** The N<sub>2</sub>-sorption analysis revealed the porosity and textural properties of IMo<sub>6</sub>@iPAF-1 at 77 K (a)(b), IR (c), after the fifth and ninth cycle and SEM (d) after the reaction.

**Fig. S14** The diesel and gasoline before the reaction (left) and after (right) treatment.

**Scheme S1** The interaction of between IMo<sub>6</sub>O<sub>24</sub><sup>5-</sup> and proton attached nitrogen in imidazole.

**Table S1** The element contents of IMo<sub>6</sub>@iPAF-1.

**Table S2** The summary of porosity measurements for IMo<sub>6</sub>@iPAF-1 after the fifth and ninth cycle

## Materials and Methods

### Physical measurements

IR spectra (4000–400  $\text{cm}^{-1}$ ) were recorded in KBr disks on a Nicolet Magna 560 IR spectrometer. UV-Vis spectra (200–800 nm) were recorded on a Cary 500 UV-Vis-NIR spectrophotometer. DR-UV-Vis spectra (200–800 nm) were obtained on a UV-2600 UV-Vis spectrophotometer (Shimadzu). The UV-visible spectra were recorded on T1810. XPS were recorded on an Escalab-MK II photoelectronic spectrometer with Al  $K\alpha$  (1200 eV). Thermogravimetric (TGA) curve was done with a SDT Q600 instrument from 16 °C to 800 °C at a scan rate of 0.5 °C·min<sup>-1</sup>. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy were performed using a XL30 ESEM FEG at 25 kV (PhilipsXL-30). The Electron Paramagnetic Resonance (EPR) were obtained by JES FA300 spectrometer, with a resonance frequency of 9.05 GHz, microwave power of 0.998 mW, modulation frequency of 100 kHz, modulation amplitude of 1×0.1 mT, sweep width of 5×1 mT, time constant of 0.03 s, sweep time of 60 s. EDX was performed to take into account of the I, Na, Mo, C, N, Cl, S, and O elements. Raman spectroscopy was performed using a Renishaw-UV-vis Raman System 1000 equipped with a CCD detector at room temperature. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. The XRD patterns of the samples were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.154178$  nm). The identification and quantification of DBT, 4,6-DMDBT, BT and thiophene in decalin were performed by Gas Chromatography (GC). [1] The oxidative reaction product was determined by GC–MS (HP 6890 GC-5973MSD). The sulfur content in real diesel

was tested by ICP-AES (ICAP 6300). The  $\text{SO}_4^{2-}$  was tested by Ion chromatography. (Thermo Scientific ICS-1600). Gas flowmeter was tested by D08-1F&1FP Flow Readout Box.( Beijing Sevenstar Flow Co., Ltd )

## Materials

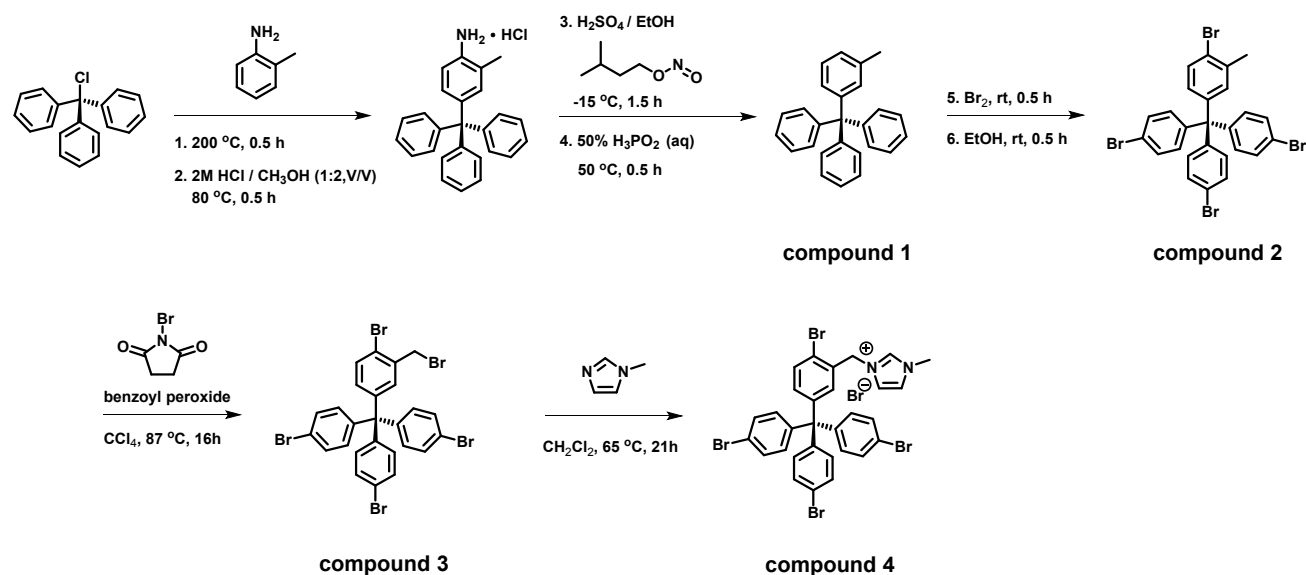
All starting materials and organic solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. All reactions were performed in oven-dried glassware under nitrogen or argon atmosphere using standard Schlenk and glovebox techniques. The polyoxometalate,  $\text{Na}_5\text{IMo}_6\text{O}_{24}$ , was prepared according to Ref. S1 and characterized by IR spectroscopy.[2]

## General instrumentation and methods

$^1\text{H}$  NMR spectra were recorded on Varian Inova 500 MHz NMR spectrometer. FT-IR measurements were performed on the Nicolet IS50 Fourier transforms infrared spectrometer. TGA was measured on the METTLER-TOLEDO TGA/DSC 3+ analyzer at the  $10\text{ }^\circ\text{C min}^{-1}$  heating rate in air atmosphere. The Elemental analysis (for C, H, and N) was measured using an EA3000 Analyzer.  $\text{N}_2$ -adsorption isotherms and pore size distribution were obtained at 77 K using an Autosorb iQ2 adsorptometer, Quantachrome Instrument. SEM and EDS were implemented on the field emission scanning electron microscopy (FE-SEM, SU-8010, Hitachi). PXRD measurements were carried out on the Rigaku SmartLab X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation (40 kV, 30 mA,  $\lambda = 1.5418\text{ \AA}$ ) and a scanning step of  $0.01^\circ$ . The catalytic reaction product was determined by GC-MS (HP 6890GC-5973MSD). The identification and quantification of organic sulfur in decalin were performed by Gas Chromatography (GC) coupled with a flame ionization detector (Agilent 7820A) equipped with a capillary column (HP-5,  $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) under the following analytical conditions: split ratio, 1/100; carrier gas, ultra-purity nitrogen with column flow of 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  $\mu\text{l}$ . To detect dibenzothiophene and 4,6-dimethyldibenzothiophene: injection port temperature,  $240\text{ }^\circ\text{C}$ ; detector temperature,  $250\text{ }^\circ\text{C}$ ; oven temperature,  $150\text{ }^\circ\text{C}$  hold for 4 min, to  $230\text{ }^\circ\text{C}$  at  $50\text{ }^\circ\text{C/min}$ , hold for 6.4 min.

## Synthetic Procedure

The monomers (compounds 1-4) and iPAF-1 were synthesized according to the previous work.[3]



Schematic route (a) to the synthesis of the monomers (compounds 1-4).

### Synthesis of compound 1

Trityl chloride (9.2 g, 32.9 mmol) and o-toluidine (9.4 mL, 88.8 mmol) were added into a 250 mL round-bottom flask. This mixture was stirred and refluxed for 0.5 h. After that, the resulting purple slurry reaction mixture was allowed to cool to room temperature. A mixture of 2M HCl and methanol (25 mL/50 mL) was poured into the flask and the solid was grounded into powder with a spatula. The mixture was then heated at 80 °C for 0.5 h. After cooling to room temperature, the reaction mixture was filtered and washed with DI H<sub>2</sub>O (125 mL) to afford a light purple solid.

The light purple solid was added to the mixed solution of ethanol (65 mL) and concentrated H<sub>2</sub>SO<sub>4</sub> (10 mL, 96 wt%). After cooling down to -15 °C, isoamyl nitrite (7.5 mL, 55.8 mmol) was then added slowly over a 10 min period. The resulting mixture was stirred at -15 °C for 1 h. At this temperature, aqueous hypophosphoric acid (15 mL, 50%) was added to the reaction mixture and then was stirred at 50 °C for 2 h. The resultant precipitate was collected by filtration and washed with DI H<sub>2</sub>O (100 mL) and ethanol (100 mL). The tan brown crude product **compound 1** (8.6 g, 25.6 mmol, 78%) was collected without any further purification. <sup>1</sup>H NMR (499.8 MHz, CDCl<sub>3</sub>): δ

2.26 (3H, CH<sub>3</sub>), 7.00 (1H, Ar-H), 7.01 (1H, Ar-H), 7.03 (1H, Ar-H), 7.14 (1H, Ar-H), 7.18 to 7.25 (15H, trityl Ar-H).

### Synthesis of compound 2

Compound 1 (3.0 g, 8.96 mmol) was added in a 250 mL 2-neck round-bottom flask equipped with a magnetic stir bar. One of the two necks was fitted with a rubber septum and the other one was then fitted with an exhaust gas-guide tube into the aqueous solution of NaOH. Neat bromine (3.5 mL, 67.3 mmol) was added dropwise through the septum via a syringe within 5 minutes. The resulting solution was allowed to stir at room temperature for 0.5 h. Ethanol (60 mL) was then added to the reaction mixture and stirred for an additional 0.5 h. The resultant precipitate was collected by filtration and washed with 150 mL of ethanol. The collected crude product was then purified by column chromatography to afford **compound 2** (4.9 g, 7.6 mmol, 85%) as a white solid. <sup>1</sup>H NMR (499.8 MHz, CDCl<sub>3</sub>): δ 2.30 (3H, CH<sub>3</sub>), 6.80 (1H, Ar-H), 6.98 (1H, Ar-H), 7.02 (6H, trityl Ar-H), 7.38 (6H, trityl Ar-H), 7.41 (1H, Ar-H).

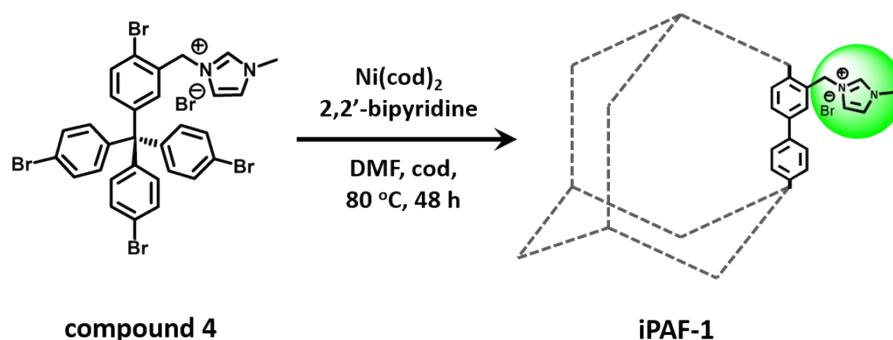
### Synthesis of compound 3

Compound 2 (1.0 g, 1.53 mmol), N-bromosuccinimide (0.356 g, 1.99 mmol) and benzoyl peroxide (0.010 g, 0.04 mmol) were dissolved in anhydrous CCl<sub>4</sub> (40 mL) and refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the filtrate was concentrated under reduced pressure to give pale yellow oil. The off-white powder was precipitated by adding 25 mL ethanol into to the pale yellow oil under continuous sonication. The collected crude product was purified by column chromatography to afford **compound 3** (2.6 g, 4.0 mmol, 45%) as an off-white powder. <sup>1</sup>H NMR (499.8 MHz, CDCl<sub>3</sub>): δ 4.49 (2H, CH<sub>2</sub>Br), 6.93 (1H, Ar-H), 7.01 (6H, trityl Ar-H), 7.23 (1H, Ar-H), 7.41 (6H, trityl Ar-H), 7.47 (1H, Ar-H).

### Synthesis of compound 4

Compound 3 (1.0 g, 1.53 mmol) and N-methylimidazole (0.356 g, 1.99 mmol) was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and refluxed overnight. The reaction mixture was cooled to room temperature and filtered. The white powder was washed with ethyl acetate, which was collected by filtration and dried under vacuum to afford **compound 4** (1.10 g, 1.5 mmol, 98%). <sup>1</sup>H NMR (499.8 MHz,

CDCl<sub>3</sub>): δ 3.87 (3H, CH<sub>3</sub>), 5.45 (2H, CH<sub>2</sub>Br), 6.94 (1H, Ar-H), 7.06 (6H, trityl Ar-H), 7.09 (1H, Ar-H), 7.52 (6H, trityl Ar-H), 7.60 (1H, Ar-H), 7.70 (2H, Imidazol-H), 9.08 (1H, Imidazol-H).



Schematic route (b) to the synthesis of the iPAF-1.

### Synthesis of iPAF-1

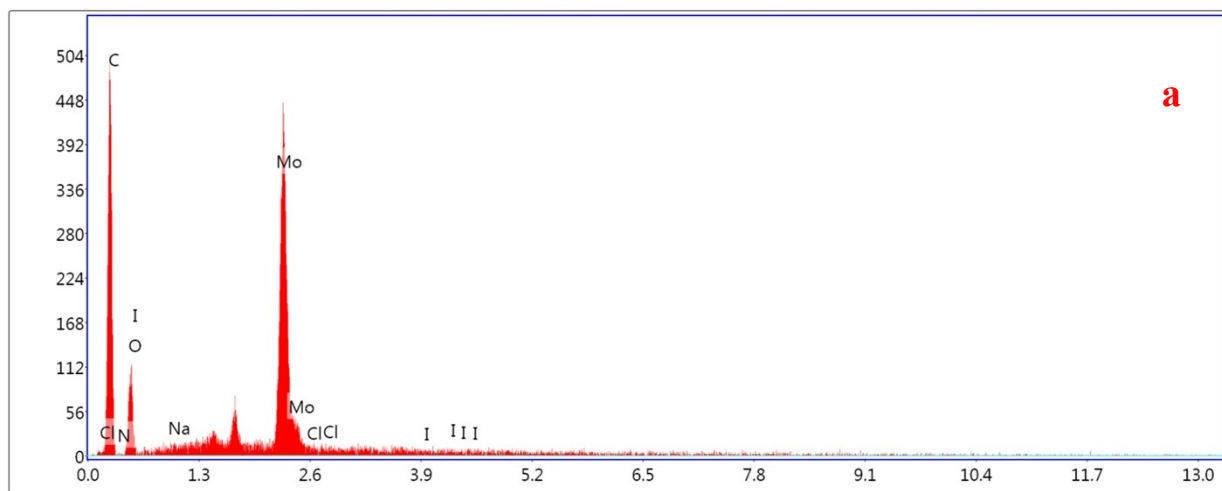
The bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)<sub>2</sub>], 2.25 g, 8.18 mmol), 2,2'-bipyridyl (1.28 g, 8.18 mmol) and 1,5-cyclooctadiene (cod, 1.05 mL, 8.32 mmol) were dissolved in anhydrous DMF (120 mL) under Argon atmosphere. Then the resulting purple solution was heated at 80 °C for 1 h. After that, compound 4 (1.27 g, 1.57 mmol) was added and the reaction mixture was stirred for 48 h at 80 °C to give a deep purple suspension. After cooling to room temperature, concentrated HCl was added to the mixture. The residue was filtrated and washed with 6 M HCl (three times), DI H<sub>2</sub>O (three times) and THF (once) respectively, to afford a light yellow powder that was then Soxhlet extracted with THF for 48 h (576 mg, 81% yields).

[1] X. Yu, M. Shi, S. Yan, H. Wang, X. Wang, W. Yang, Designation of choline functionalized polyoxometalates as highly active catalysts in aerobic desulfurization on a combined oxidation and extraction procedure, *Fuel*, 207 (2017) 13-21.

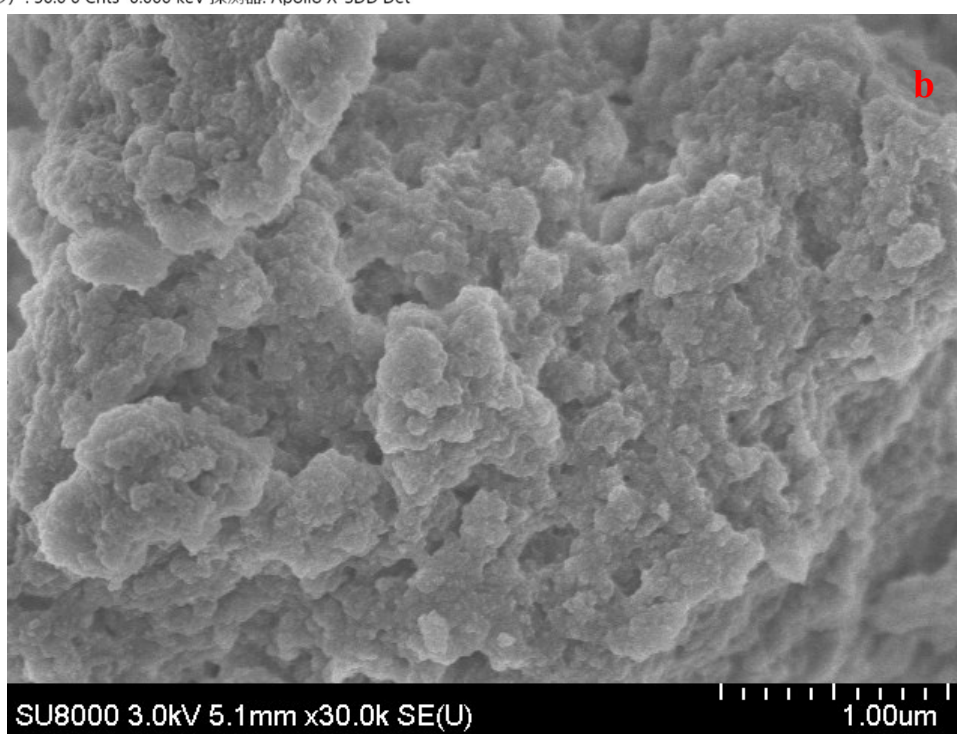
[2] S.-y. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, An efficient aerobic oxidation of various organic compounds catalyzed by mixed addenda heteropolyoxometalates containing molybdenum and vanadium, *J. Mol. Catal. A: Chem.*, 110 (1996) 105-117.

[3] Y. Tian, J. Song, Y. Zhu, H. Zhao, F. Muhammad, T. Ma, M. Chen, G. Zhu, Understanding the desulphurization process in an ionic porous aromatic framework, *Chem. Sci.*, 10 (2019) 606-613.

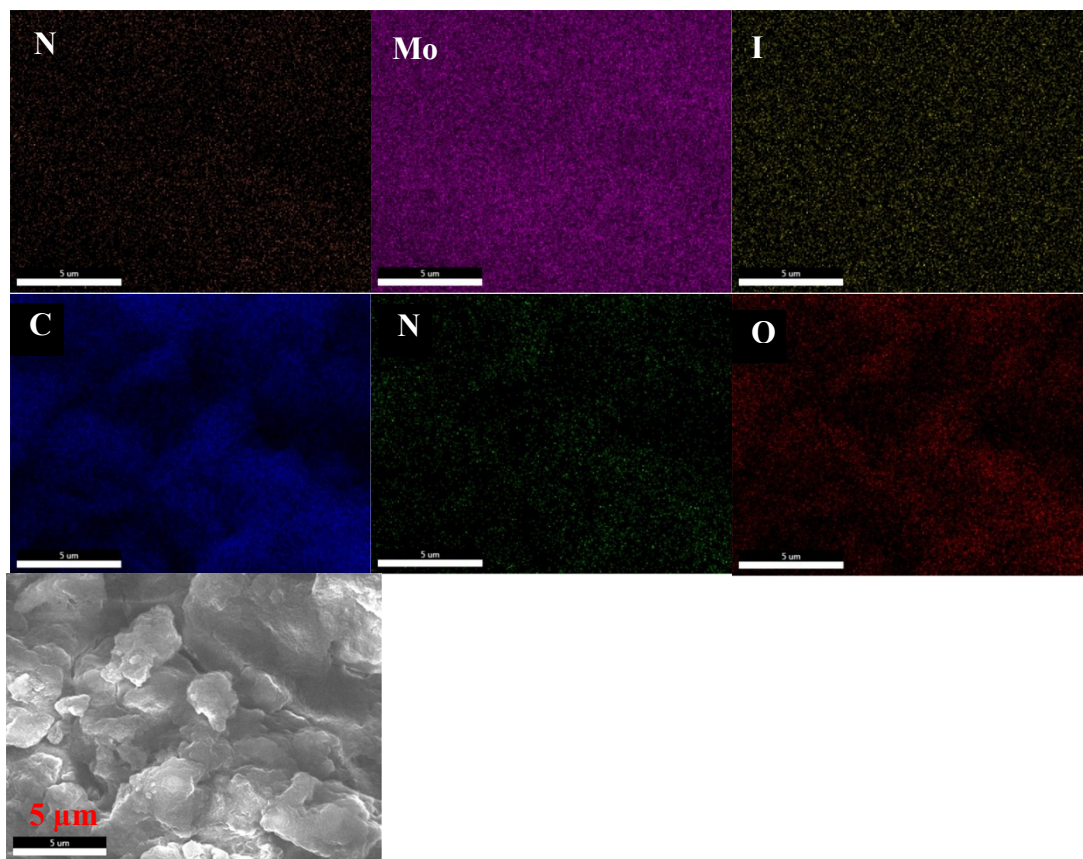




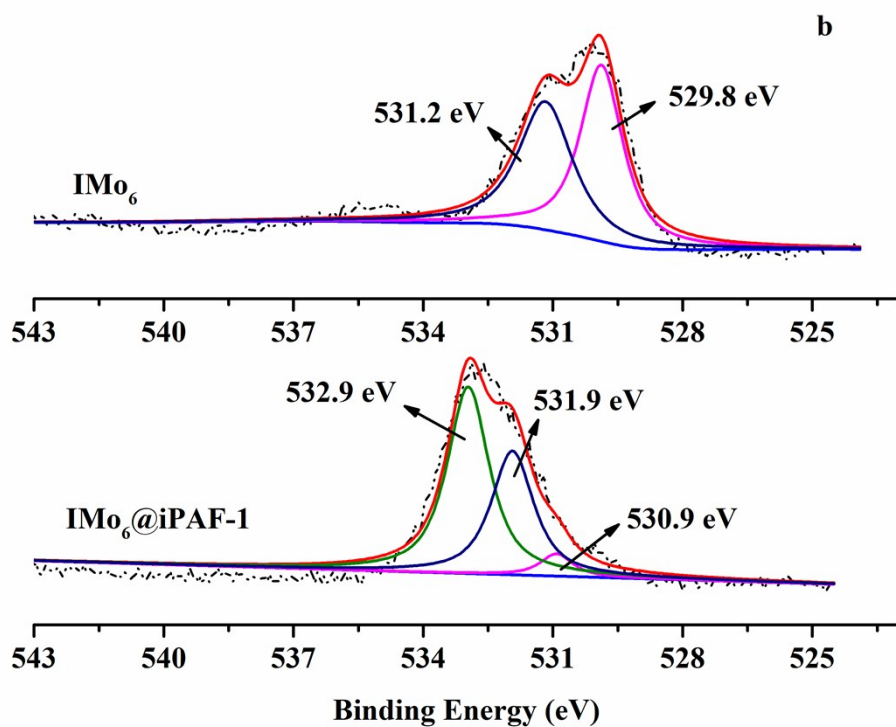
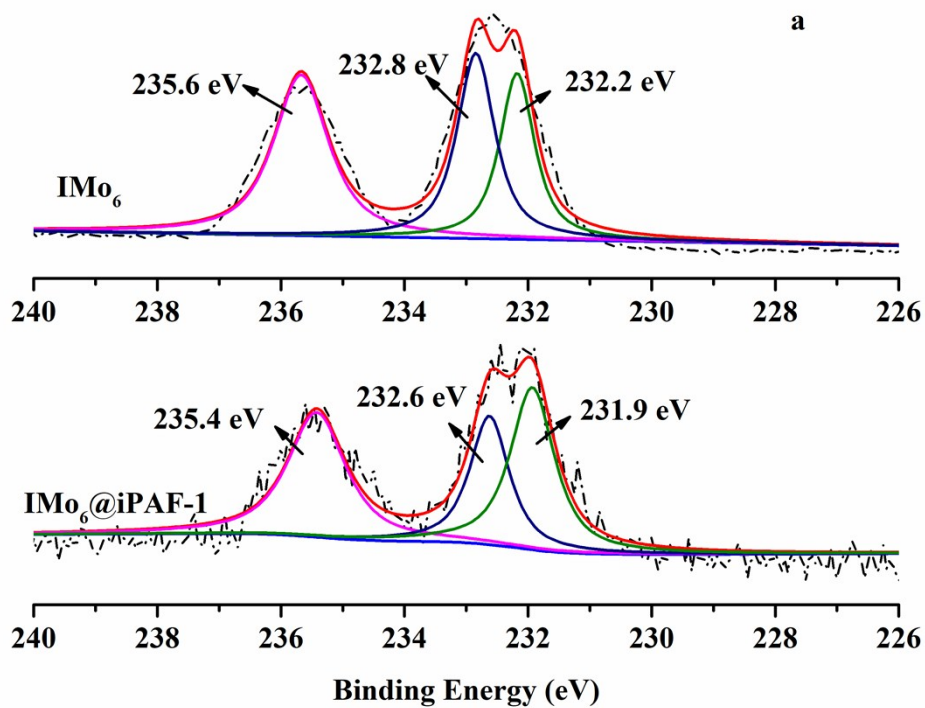
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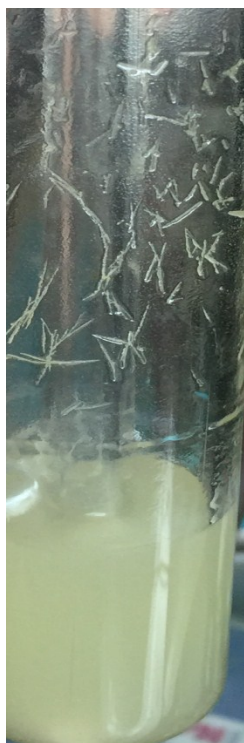
**Fig. S1** EDAX elemental analyses of and SEM of IMo<sub>6</sub>@iPAF-1.



**Fig. S2** The EDS mapping of iPAF-1 loaded with IMo6. (Color code: Brownish red: Na; Pink: Mo; Yellow: I; Blue: C; Green: N; and Red: O).

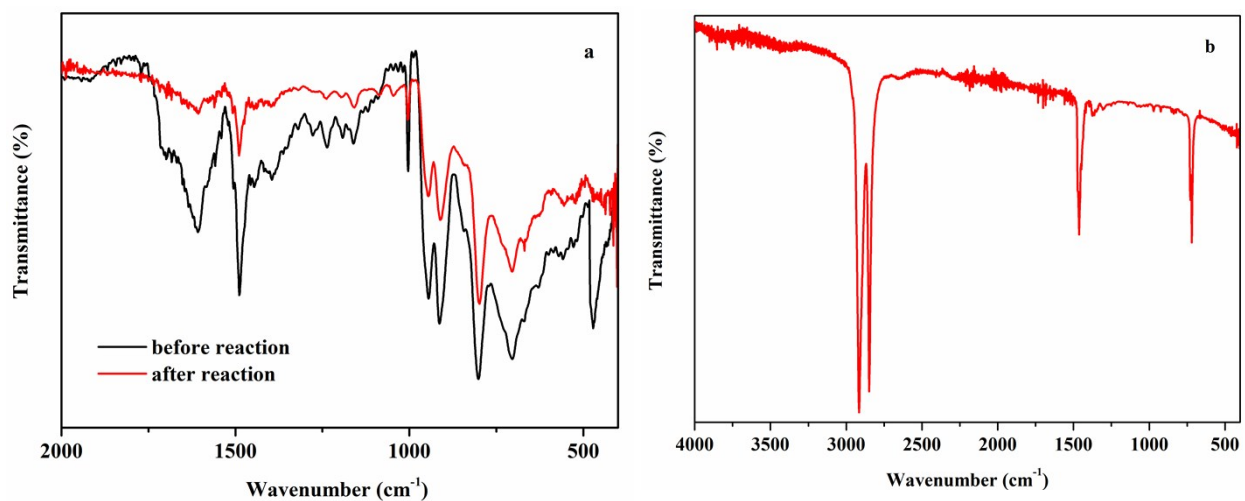


**Fig. S3** The XPS spectra of Mo3d of IMo<sub>6</sub> and IMo<sub>6</sub>@iPAF-1 (a), O1s of IMo<sub>6</sub> and IMo<sub>6</sub>@iPAF-1 (b).

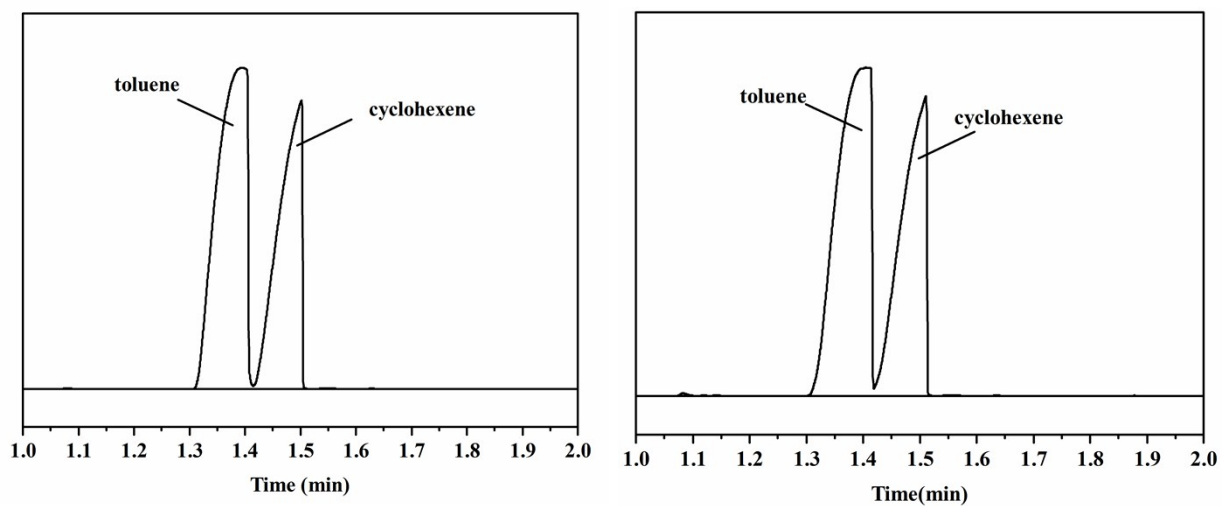


**Fig. S4** Photo image of white needle crystals deposited from the decalin with the catalyst

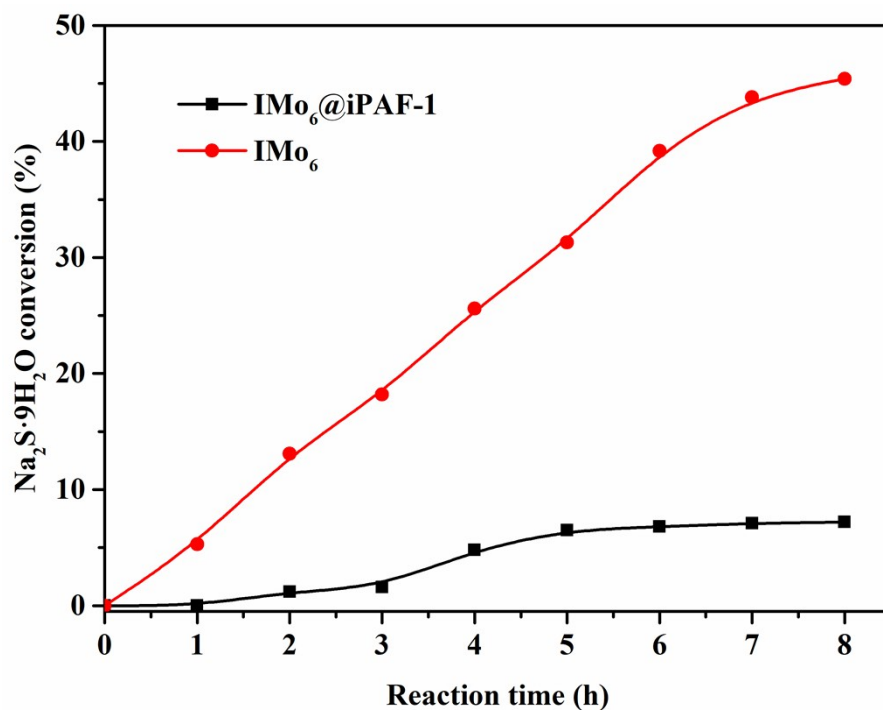
IMo<sub>6</sub>@iPAF-1.



**Fig. S5** FT-IR spectra of IMo<sub>6</sub>@iPAF-1 before reaction and after reaction (a), post-reaction solution (b).

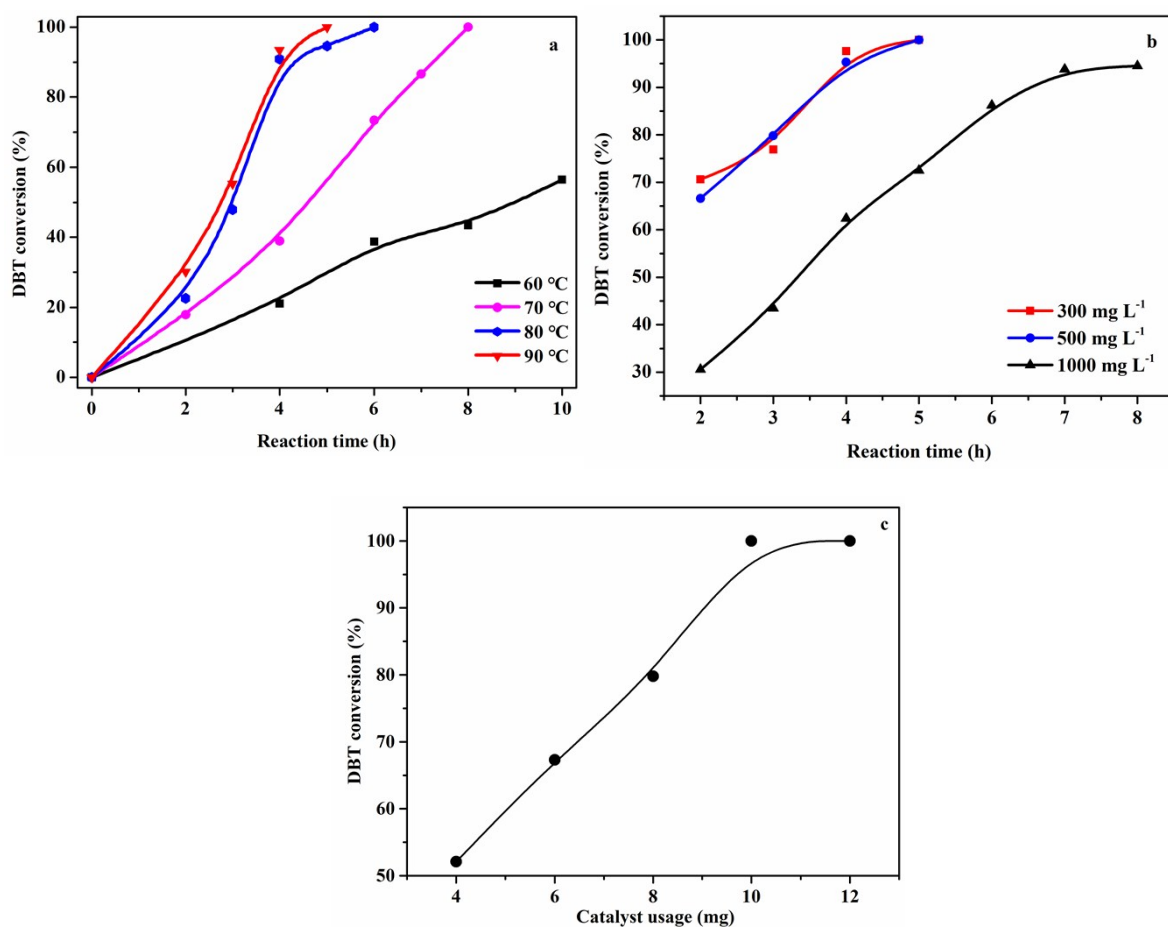


**Fig. S6** GC-FID chromatogram for the oxidation of cyclohexene and toluene. The left curve shows the chromatogram before oxidation; The right curve shows the chromatogram after oxidation. Reaction conditions: 10 mg of catalyst, oxidant O<sub>2</sub>, 90 °C for 5 h.



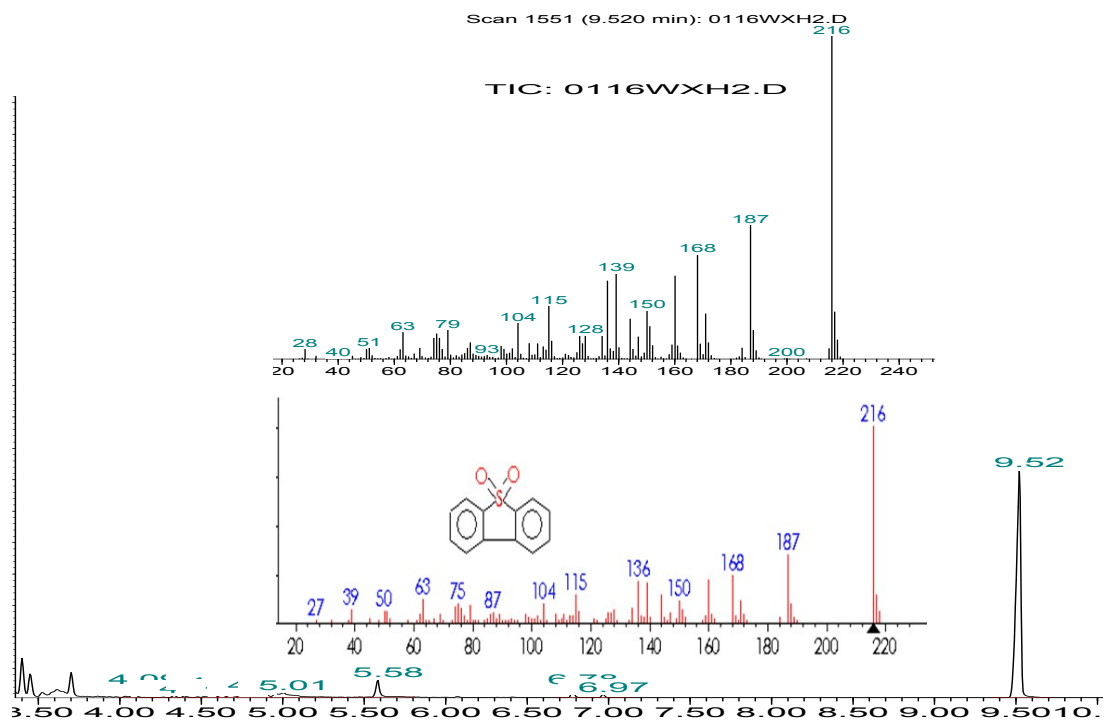
**Fig. S7** Aerobic oxidation of S<sup>2-</sup> in the presence of IMo<sub>6</sub>@iPAF-1 under their reaction conditions

as: Na<sub>2</sub>S ·9H<sub>2</sub>O (0.1mmol, 10 mL H<sub>2</sub>O), catalyst (10 mg) at 80 °C with O<sub>2</sub>.

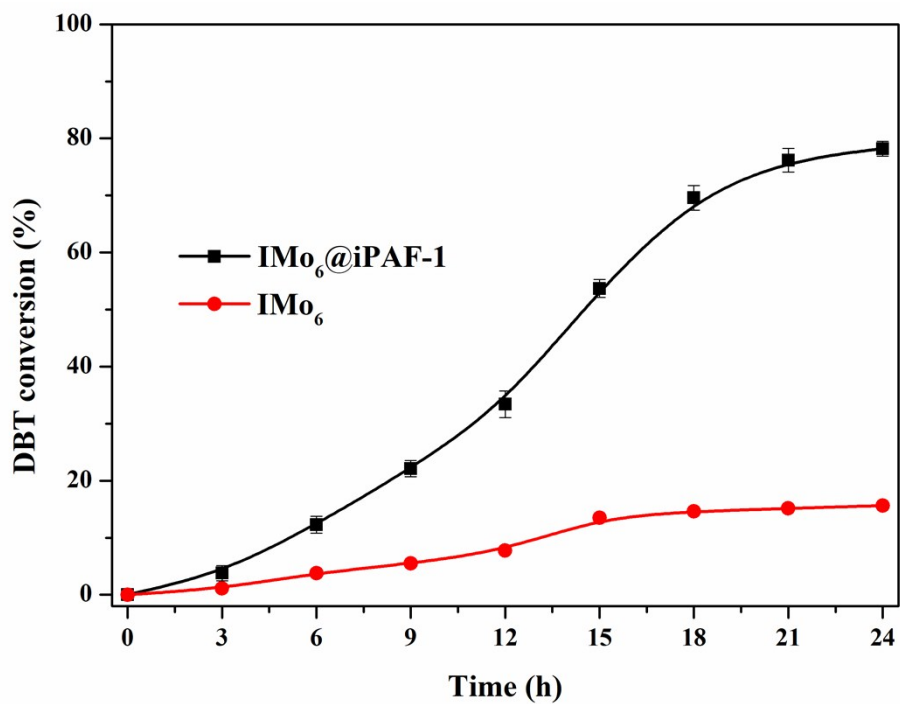


**Fig. S8** Main parameters on DBT conversion: (a) Different reaction temperatures (b) Concentration of substrate and (c) Usage of catalysts.

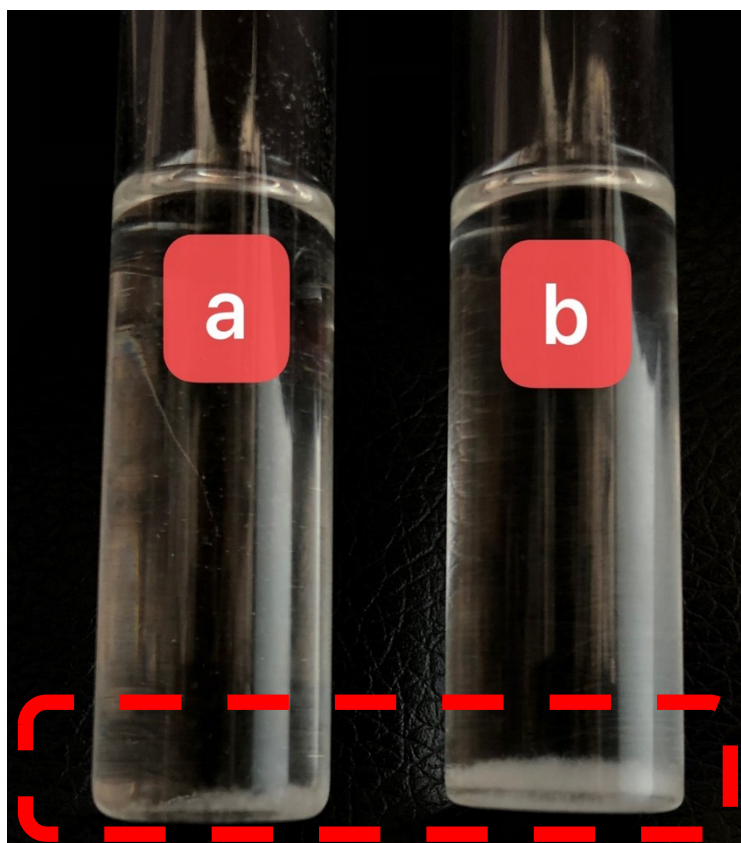




**Fig. S9** GC-MS spectrum of the reaction product (dibenzothiophene sulfone).

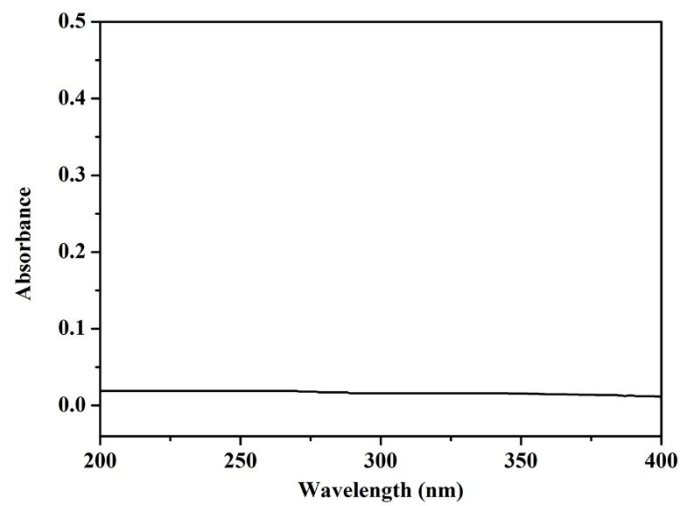


**Fig. S10** DBT in the presence of different catalysts (10 mg) at 120 °C with air for 24 h.

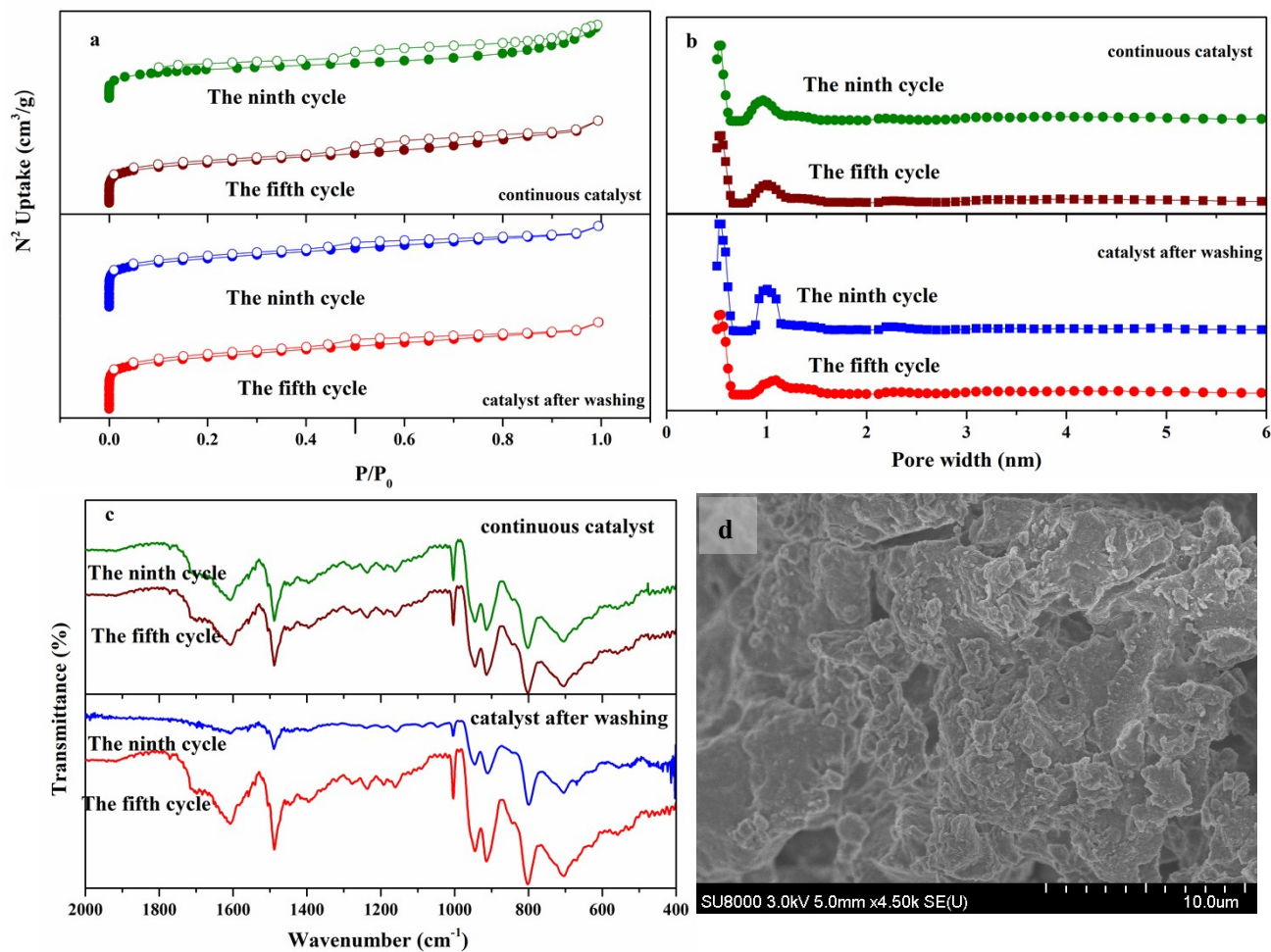


**Fig. S11** Photo image of white needle crystals deposited from the decalin with the catalyst (a)

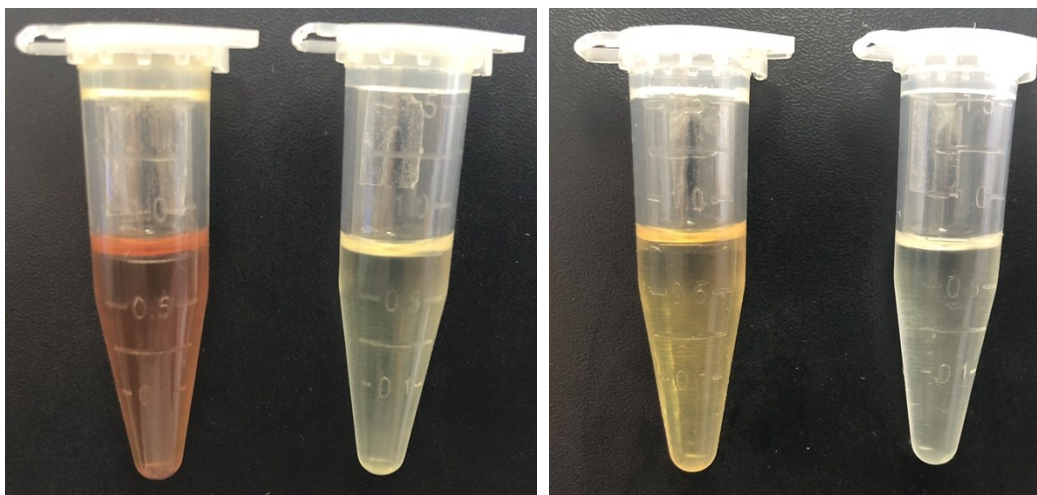
(b)  $\text{IMo}_6@\text{iPAF-1}$ .



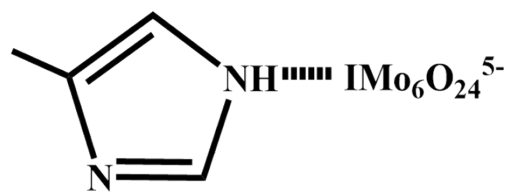
**Fig. S12** UV-Vis spectrum of IMo<sub>6</sub>@iPAF-1 dissolved in decalin.



**Fig. S13** The N<sub>2</sub> sorption isotherms for IMo<sub>6</sub>@iPAF-1 at 77 K (a)(b), IR (c), after the fifth and ninth cycle and SEM (d) after the reaction.



**Fig. S14.** The diesel and gasoline before the reaction (left) and after (right) treatment.



**Scheme S1** The interaction of between  $\text{IMo}_6\text{O}_{24}^{5-}$  and proton attached nitrogen in imidazole.

**Table S1** The element contents of IMo<sub>6</sub>@iPAF-1.

Element	C	N	O	Mo	Cl	I	Na
Atom %	51.17	3.86	17.75	21.59	0.06	4.47	1.1

**Table S2** XPS elemental distribution (at%) in various catalysts.

Sample	C1s	N1s	O1s	Mo3d	Cl2p	I3d
iPAF-1	83.73	4.65	-	-	1.78	-
IMo <sub>6</sub> @iPAF-1	52.25	4.06	20.79	18.8	-	4.1

**Table S3** The summary of porosity measurements for IMo<sub>6</sub>@iPAF-1 after the fifth and ninth cycle.

Samples	S <sub>BET</sub> * [m <sup>2</sup> g <sup>-1</sup> ]	Pore size [nm]	Pore volume [cc g <sup>-1</sup> ]
fifth continuous IMo <sub>6</sub> @iPAF-1	510	0.54,1.00	0.322
ninth continuous IMo <sub>6</sub> @iPAF-1	498	0.54,0.96	0.319
fifth washing IMo <sub>6</sub> @iPAF-1	513	0.54,1.050	0.325
ninth washing IMo <sub>6</sub> @iPAF-1	505	0.54,1.00	0.319

\*S<sub>BET</sub> denotes BET surface areas.