

## Supporting Information

### **Phosphotungstic acid encapsulated in the mesocages of amine-functionalized metal-organic framework for catalytic oxidative desulfurization**

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## **Catalyst preparation**

### **Synthesis of MIL-101(Cr)-NO<sub>2</sub>**

MIL-101(Cr)-NO<sub>2</sub> was synthesized in a hydrothermal reaction of 148 mg (0.7 mmol) 2-nitroterephthalic acid and 186 mg (0.7 mmol) CrCl<sub>3</sub>·6H<sub>2</sub>O in 10 mL H<sub>2</sub>O at 180 °C for 96 h. Ultrasonic processing of reactants for half an hour before heated with the furnace, make the reactants mixed with each other more homogenously. The green product was centrifuged and washed by water for three times, then transferred into autoclaves with ethanol. The autoclaves were heated to 100 °C for 10 h, then the activated product was centrifuged and washed by ethanol for three times. By the way, we use ultrasonic while washing process, to ensure the unreacted 2-nitroterephthalic can be wipe off completely.

## **Synthesis of MIL-101(Cr)-NH<sub>2</sub>**

MIL-101(Cr)-NH<sub>2</sub> was synthesized in a 4 h reaction at 70 °C from 200 mg MIL-101(Cr)-NO<sub>2</sub> and 3 g SnCl<sub>2</sub>·2H<sub>2</sub>O in 30 mL absolute ethanol. The mixture was cooled to temperature, 15 ml concentrated HCl were added and the mixture was stirred overnight (about 10 h). The mixture was centrifuged and the solid was washed three times with H<sub>2</sub>O and one time with ethanol.

## **Distribution of DBT and DBTO<sub>2</sub> in model oil and polar solvent**

### **The procedure to investigate the distribution of DBT**

5 mL model oil and 5 mL polar phase (DMF or MeCN) were placed in a round-bottom flask (25 mL) and shook with hands. After standing for a while (1min, 5 min and 10 min), the upper layer model oil and sub-layer polar solvent were analyzed by GC.

### **The procedure to investigate the distribution of DBTO<sub>2</sub>**

For the corresponding sulfone of DBT, two ways to be used:

Method one: 50 mg PTA@MIL-101(Cr)-NH<sub>2</sub>, 100 μL H<sub>2</sub>O<sub>2</sub>, and 5 mL MeCN were added to a 25 mL round-bottom flask and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analyzed by GC. In the sub-layer (MeCN), only DBTO<sub>2</sub> was detected (monitored by GC-MS). In the upper layer (model oil),

only n-dodecane and a few amount of DBTO<sub>2</sub> (< 2 ppmw, detected by GC) were detected.

Method two: 1 mg DBTO<sub>2</sub> was added to 50 mL n-heptane and stirred. Half an hour later, most of white solid didn't dissolve. However, after 1 mL MeCN or DMF was added, the white solid dissolved instantly.

Due to high polarity of DBTO<sub>2</sub>, which enhances the DBTO<sub>2</sub> dissolving in polar solvent, the DBTO<sub>2</sub> can be almost removed completely. It can be demonstrated the higher conversion rate of DBT to sulfone, the lower residual sulfur in the model oil.

## Control experiments

### **Pure PTA as homogeneous catalyst with H<sub>2</sub>O<sub>2</sub>**

PTA (18 mg, equal to 50 mg PTA@MIL-101(Cr)-NH<sub>2</sub>), H<sub>2</sub>O<sub>2</sub> (40 μL), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC. However, the homogeneous catalyst is hard to be recycled.

### **Pure MIL-101(Cr)-NH<sub>2</sub> as catalyst with H<sub>2</sub>O<sub>2</sub>**

MIL-101(Cr)-NH<sub>2</sub> (32 mg, equal to 50 mg PTA@MIL-101(Cr)-NH<sub>2</sub>), H<sub>2</sub>O<sub>2</sub> (20, 30, 40,100μL), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC. With respect to the recycling

experiment, model oil in upper layer was cast out, then the catalyst in lower layer was collected by centrifugation and washed with MeCN for three times after the reaction.

### **No catalyst with H<sub>2</sub>O<sub>2</sub>**

H<sub>2</sub>O<sub>2</sub> (40 μL), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC.

### **Pure PTA as homogeneous catalyst without H<sub>2</sub>O<sub>2</sub>**

PTA (18 mg, equal to 50 mg PTA@MIL-101(Cr)-NH<sub>2</sub>), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC.

### **Pure MIL-101(Cr)-NH<sub>2</sub> as catalyst without H<sub>2</sub>O<sub>2</sub>**

MIL-101(Cr)-NH<sub>2</sub> (32 mg, equal to 50 mg PTA@MIL-101(Cr)-NH<sub>2</sub>), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC.

### **No catalyst without H<sub>2</sub>O<sub>2</sub>**

H<sub>2</sub>O<sub>2</sub> (40 μL), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at

temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC.

### **PTA@MIL-101(Cr)-NH<sub>2</sub> without H<sub>2</sub>O<sub>2</sub>**

PTA@MIL-101(Cr)-NH<sub>2</sub> (50 mg), and MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. After two minutes' standing, the upper layer model oil and sub-layer polar solvent were analysis by GC.

## **Characterization methods**

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku-Dmax2500 diffractometer using CuK $\alpha$  radiation ( $\lambda = 0.154$  nm). Infrared (IR) spectra were recorded on PerkinElmer Spectrum instrument in the range of 4000-400cm<sup>-1</sup> using KBr pellets. Analysis of PTA content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). The morphologies of catalysts were studied using a JEOL-2010 transmission electron microscope (TEM) working at 200 KV and a JSM6700. The samples were prepared by placing a drop of product in ethanol onto a continuous carbon-coated copper TEM grid. Scanning electron microscope (SEM) working at 10KV. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument. The gas chromatography (GC) measurements were performed on a G7890A-GC using n-dodecane as internal standard. The gas chromatography–mass spectrometry (GC-MS) measurements were performed on a Varian 450-GC/240-MS. Thermo Gravimetric (TG)

measurements were performed on a STA 449C (NETZSCH company) instrument in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>.

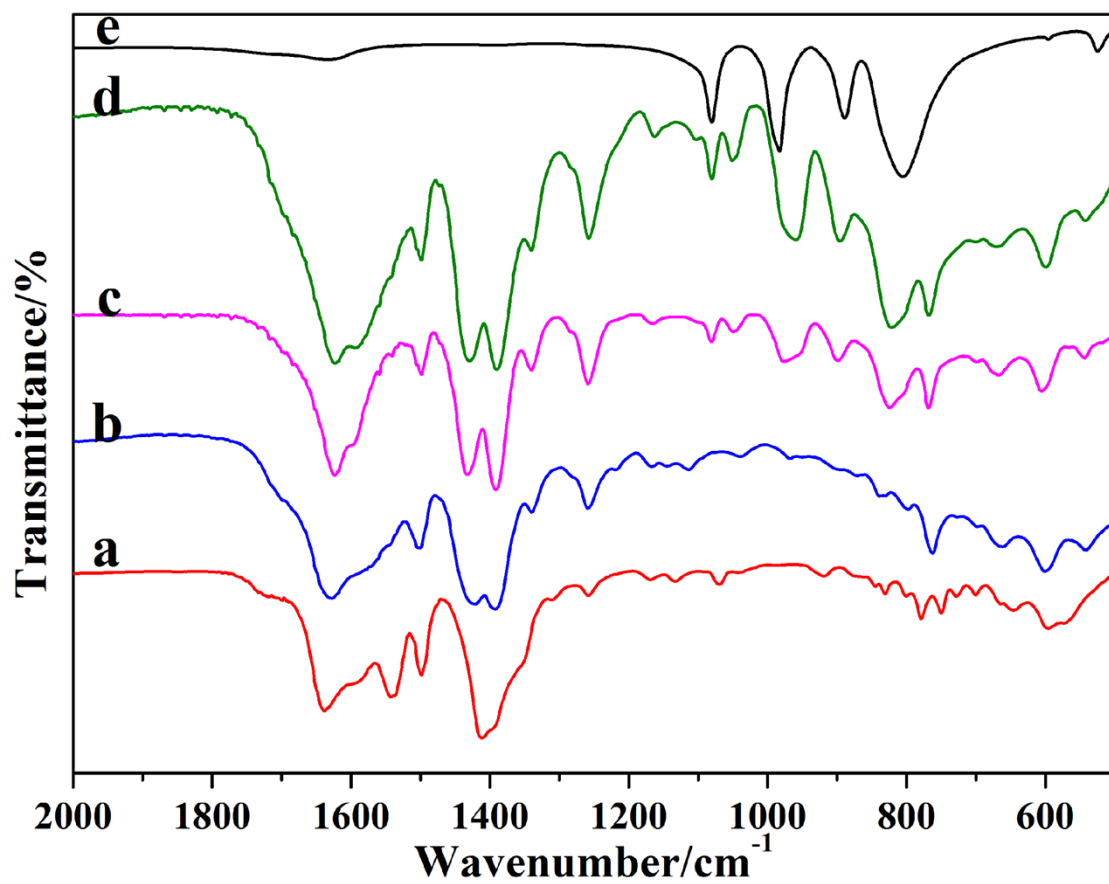


Fig. S1 FT-IR spectra of (a) MIL-101(Cr)-NO<sub>2</sub>, (b) MIL-101(Cr)-NH<sub>2</sub>, (c) PTA@MIL-101(Cr)-NH<sub>2</sub>, (d) PTA@MIL-101(Cr)-NH<sub>2</sub> after six catalysis cycles, and (e) pure PTA.

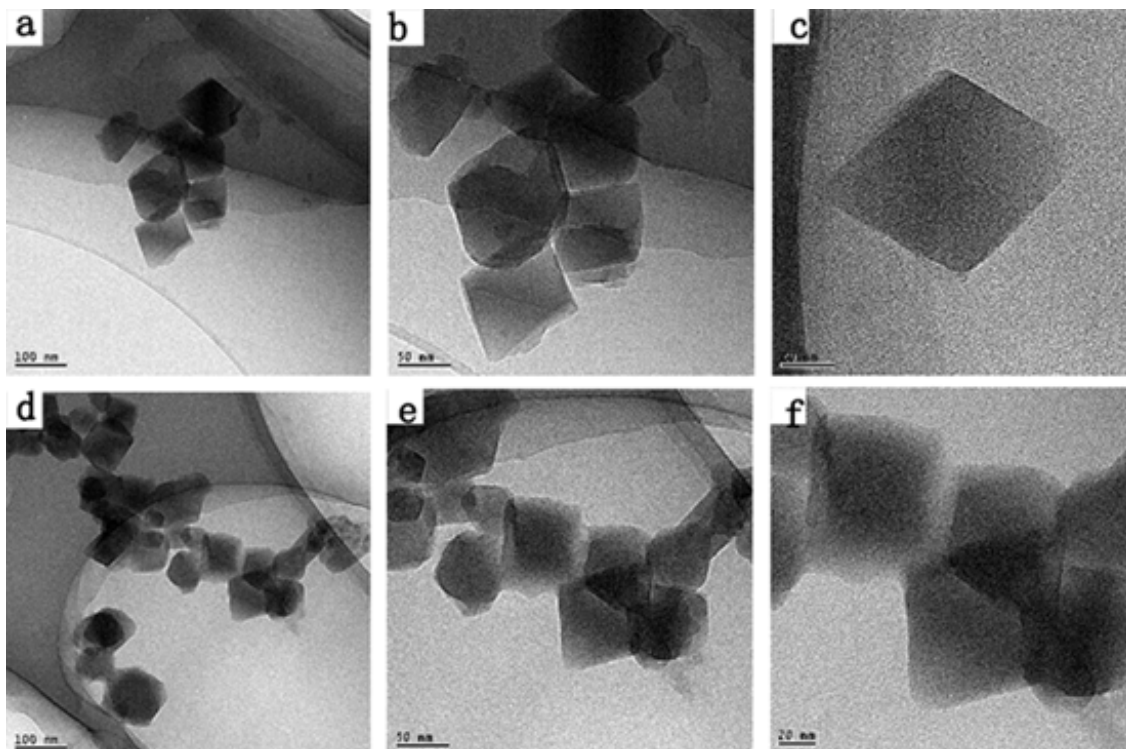
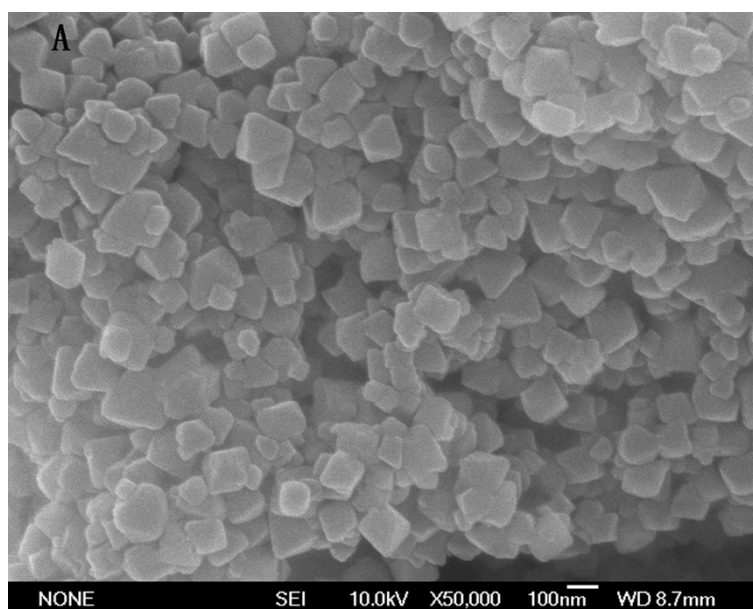
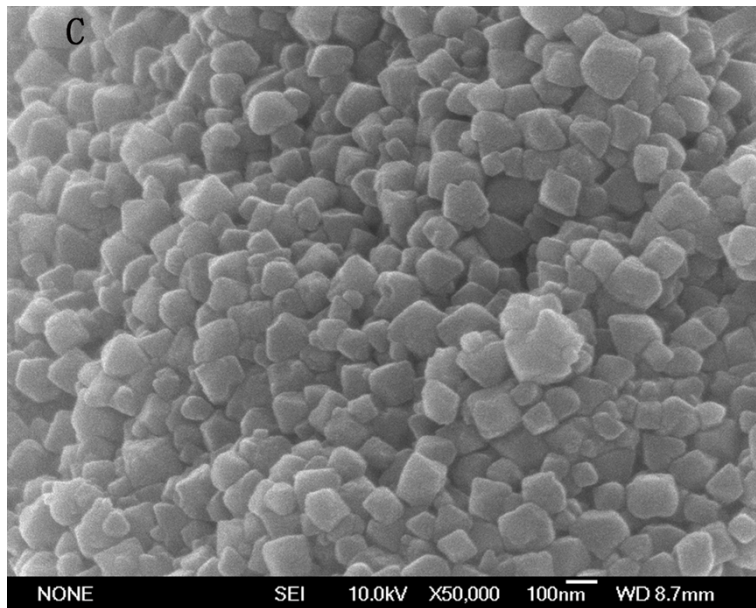
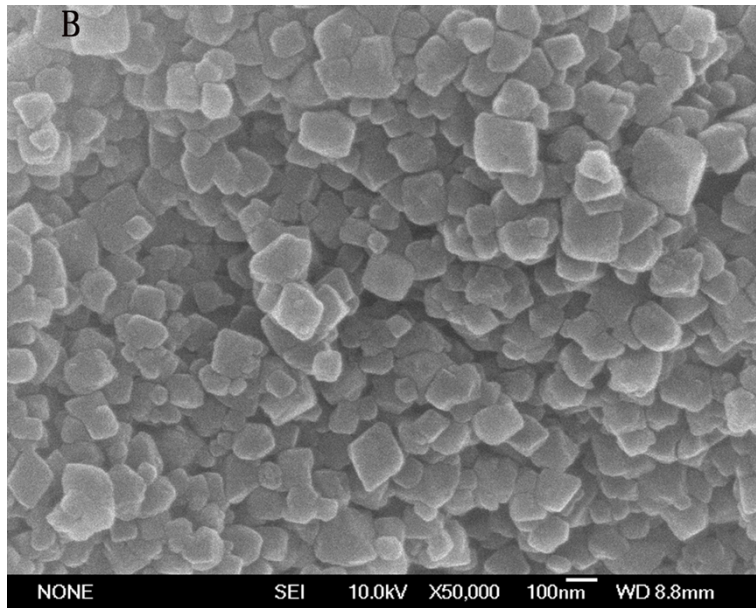


Fig. S2 (a, b, c) TEM images of MIL-101(Cr)-NH<sub>2</sub> and (d, e, f) PW<sub>12</sub>@MIL-101(Cr)-NH<sub>2</sub>.







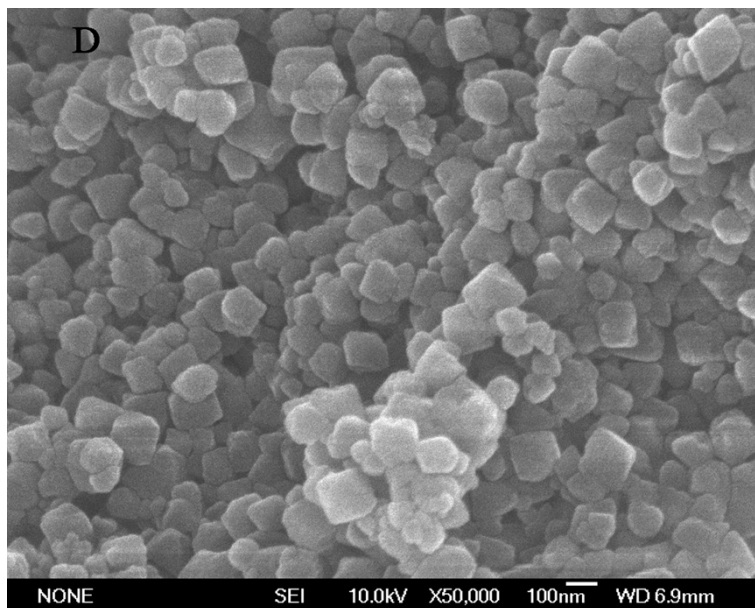


Fig. S3 (A) SEM images of MIL-101(Cr)-NO<sub>2</sub>, (B) MIL-101(Cr)-NH<sub>2</sub>, (C) PW<sub>12</sub>@MIL-101(Cr)-NH<sub>2</sub> and (D) PW<sub>12</sub>@MIL-101(Cr)-NH<sub>2</sub> after six catalysis cycles.

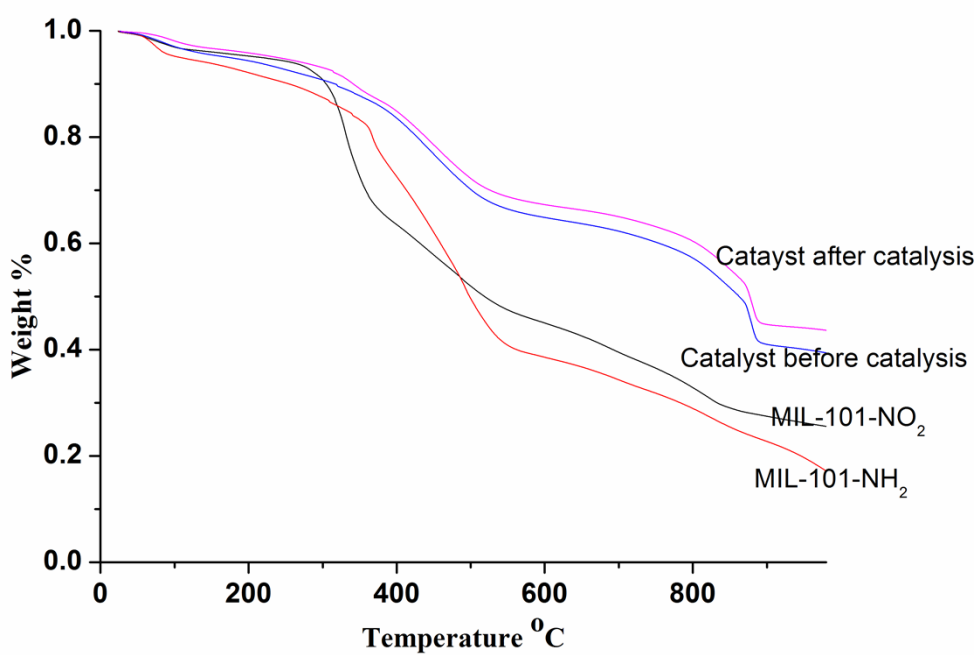


Fig. S4 Thermo Gravimetric Analysis of MIL-101(Cr)-NO<sub>2</sub>, MIL-101(Cr)-NH<sub>2</sub>, PW<sub>12</sub>@MIL-101(Cr)-NH<sub>2</sub> and PW<sub>12</sub>@MIL-101(Cr)-NH<sub>2</sub> after six catalysis cycles.

**Table S1** Control experiment at the optimal condition (Condition: temperature, 50 °C, time, 1 h, extraction and reaction solvent, MeCN.).

Entry	Catalyst	H <sub>2</sub> O <sub>2</sub> (μL)	Conversion %
1	/	/	0
2	MIL-101(Cr)-NH <sub>2</sub>	/	0
3	PTA	/	0
4	PTA@MIL-101(Cr)-NH <sub>2</sub>	/	0
5	/	40	4.79
6	MIL-101(Cr)-NH <sub>2</sub>	40	2.84
7	PTA	40	99.6
8	PTA@MIL-101(Cr)-NH <sub>2</sub>	40	100