

Linker selective retention strategy to construct hierarchical porous metal–organic frameworks with highly catalytic activity of oxidative desulfurization

Xiaowen Sun,^a Yun-Feng Gu,^b Xiao-Min Zhang,^c Yan Shen,^a Dan-Hong Wang,^a Shu-Ming Zhang,^b Mei-Hui Yu,^{* a} and Ze Chang^{* a}

a School of Materials Science Nankai University, Tianjin 300350, China

b School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China.

c College of Chemistry, Nankai University, Tianjin 300071, China.

*Corresponding authors. E-mail: mh@nankai.edu.cn (M.-H. Yu); changze@nankai.edu.cn (Z. Chang)

Experimental procedures

Chemicals

Zirconium(IV) n-propoxide (70% w/w in n-propanol), acetic acid, p-phthalic acid, and 30% hydrogen peroxide solution were purchased from Innochem. N,N-dimethylformamide, ethyl alcohol, decahydronaphthalene, dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), ethyl diazoacetate (EDA), sodium hydroxide and hydrochloric acid were purchased from Macklin. Rhodamine 6G and methyl red were purchased from J&K Scientific. CD₃CN (>99.8% atom % D) was purchased from Aladdin.

Catalyst preparation.

UiO-66: A mixed solution of 70% zirconium propoxide [Zr(O_nPr)₄] solution in 1-propanol (75 μL, 0.167 mmol), DMF (7 mL) and acetic acid (4 mL, 70 mmol) was added into a 20 mL glass vial. Then the solution was heated at 130 °C for 150 minutes and an obvious change from colorless to pale yellow of the solution could be observed. 75 mg BDC was added into the precursor and ultrasonic treatment until mixing uniformly. Then the glass vial was put into a shaking incubator with the temperature of 25 °C and 220 rpm reacting for 2 days. Finally, the UiO-66 powder was treated at 250 °C with a heating rate of 5 °C min⁻¹ for 2 hours under nitrogen atmosphere.

UiO-660-dhtz (BDC/dhtz = 1:1) A mixed solution of 70% zirconium propoxide [Zr(O_nPr)₄] solution in 1-propanol (75 μL, 0.167 mmol), DMF (7 mL) and acetic acid (4 mL, 70 mmol) was added into a 20 mL glass vial. The solution was heated at 130 °C for 150 minutes and an obvious change from colorless to pale yellow of the solution could be observed. After cooling to room temperature, a mixture of 37 mg BDC and 38 mg dhtz was added into the precursor and ultrasonic treatment until mixing uniformly. Then the glass vial was put into a shaking incubator with the temperature of 25 °C and 220 rpm reacting for 5 days. During the shaking, the mixture color varies from dark brown to pale yellow. The pale yellow powder crystals were obtained after washing three times with DMF and dichloromethane, respectively.

UiO-660-dhtz (dhtz:BDC = 1:2) All steps were as same as UiO-660-dhtz (BDC:dhtz = 1:1), except the 37 mg BDC and 38 mg dhtz were instead of 50 mg BDC and 25 mg dhtz.

UiO-660-dhtz (dhtz:BDC = 1:3) All steps were as same as UiO-660-dhtz (BDC:dhtz = 1:1), except the 37 mg BDC and 38 mg dhtz were instead of 56 mg BDC and 19 mg dhtz.

Hierarchically porous UiO-66-dhtz (HP-UiO-66-dhtz) The UiO-66-dhtz powder was treated at 250 °C with a heating rate of 5 °C min⁻¹ for 2 hours under nitrogen atmosphere.

Oxidative Desulfurization (ODS) process of DBT and 4,6-DMDBT

0.0505 g DBT (or 4,6-DMDBT) was dissolved in 100 g decalin to obtain a 500 ppm DBT (or 4,6-DMDBT) solution as a simulated model oil (MD 500). In ODS reaction, 10 g of model oil was added into a 50 mL round bottom flask, then the 30% H₂O₂ solution was added as oxidant with O/S (one oxygen atom in H₂O₂/one sulfur atom in DBT or 4,6-DMDBT) molar ratio of 12 under stirring to form a uniform mixture and heating to the 60 °C. 100 mg catalyst was added to the above solution, the ODS reaction continued for about 180 min. The quantification of oxidation products was conducted by means of GC-2014C fitted out with a flame ionization detector (FID), using a 30 * 0.32 mm ID AC1*0.25 µm film thickness column and nitrogen as carrier gas.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using Rigaku MiniFlex600 X-ray diffraction meter in a 2θ range of 3-50° at 40 kV and 15 mA with a Cu-target tube (λ = 0.154178 nm.). The **UV/vis spectra** were measured by Persee TU-1950, BaSO₄ powder as reference sample, measuring from 300-800 nm. **TG-DTA** was measured by Thermo plus EVO2. **The specific surface areas determination and pore analysis** were performed on a Micrometrics ASAP 2460 gas adsorption analyzer and determined by the Brunauer-Emmet-Teller (BET) and the Barrett-Joyner-Halenda (BJH) method. Before the measurements, the supercritical dried samples were activated under high vacuum (less than 10⁻⁵Torr) at 40 °C. About 100 mg activated samples were used for gas sorption measurements. Adsorption isotherms were collected at 77 K with a liquid nitrogen bath. **Elemental analyzer** (Vario EL cube) was utilized to confirm the contents of N element. **FTIR spectra** were recorded on a Nicolet iS50 spectrometer (Thermo-Scientific) equipped with a MCT detector (64 scans; 8 cm⁻¹ resolution). Pure samples were pressed into self-supporting wafers. Prior to introduction of CD₃CN to the cell, samples were activated in situ under vacuum at 150 °C for 3 hours. After activation, the samples were cooled down to room temperature, and spectra at this temperature were taken as reference spectra. CDCN₃ were dragged in by argon gas for 1 hour, followed by evacuation under vacuum (1 mbar) for 40 min. Then the spectra of the samples with

CD₃CN were recorded. The spectra of CD₃CN chemisorption on MOFs were obtained by the subtraction of the reference spectra from the spectra of the samples with CD₃CN.

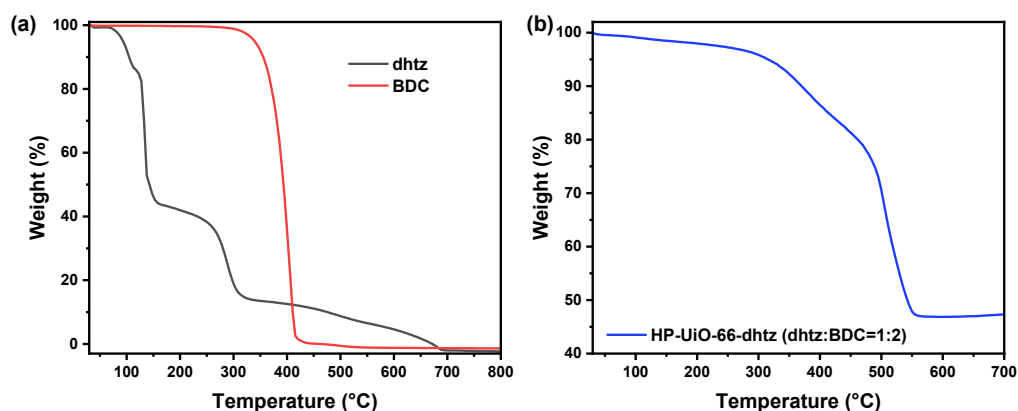


Figure S1. TGA curves of (a) dhtz and BDC; (b) HP-UiO-66-dhtz (dhtz:BDC=1:2)

According to Figure 1c, it is obvious that the m_{ZrO_2} of UiO-66-dhtz (dhtz:BDC=1:2) and UiO-66 are 34% and 48%, respectively. Considering the BDC and dhtz has similar molecular weight (166 vs. 168), it implied that the UiO-66-dhtz (dhtz:BDC=1:2) have much more cluster defects than UiO-66, the remained content metal cluster is calculated to be 71% compared to UiO-66. According to the TGA curve of dhtz (the decomposition temperature of dhtz is 60 °C) and HP-UiO-66-dhtz in Figure S1, we use the formular below to estimate the extent of missing linker defects in HP-UiO-66-dhtz:

$$M_{UiO-66-dhtz} = \frac{m_{60^\circ C}}{m_{800^\circ C}} \times 71\% \times 6M_{ZrO_2} = M_{cluster(Zr_6O_4(OH)_4)} + M_{ligand}$$

$$M_{HP-UiO-66-dhtz} = \frac{m_{60^\circ C}}{m_{800^\circ C}} \times 71\% \times 6M_{ZrO_2} = M_{cluster(Zr_6O_4(OH)_4)} + M_{ligand}$$

After calculation, the M_{ligand} of HP-UiO-66-dhtz is 64% of UiO-66-dhtz (721 and 1251, respectively), thus the extent of missing linker defects is 36%.

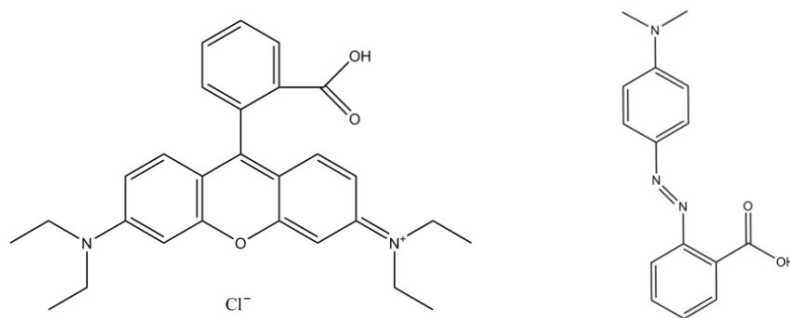


Figure S2. The structure formula of rhodamine B (size of 15.7 Å) and methyl red (size of 13 Å)

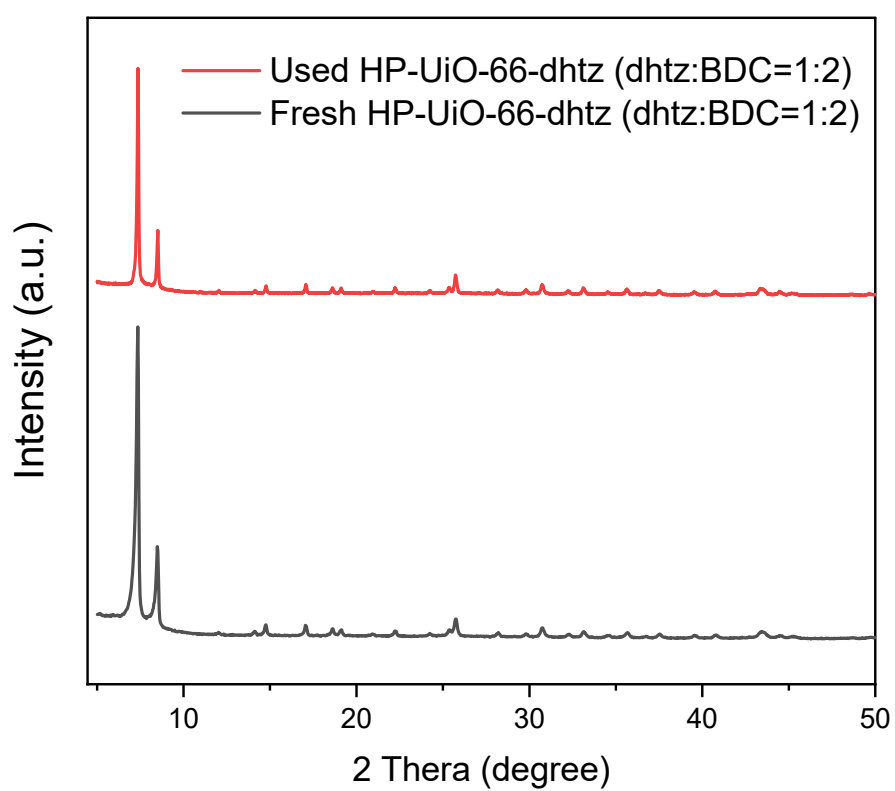


Figure S3. The PXRD patterns of HP-UiO-66-dhtz (dhtz:BDC=1:2) before and after catalytic reaction.

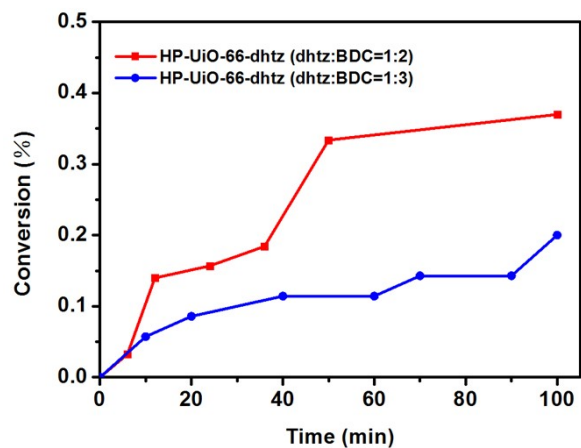


Figure S4. The ODS process of 4,6-DMDBT

Table S1. The element analysis of UiO-66-dhtz (dhtz:BDC=1:2) and UiO-66-dhtz (dhtz:BDC=1:3)

samples	N(%)	C(%)	H(%)
dhtz:BDC=1:2	2.04	28.89	2.491
dhtz:BDC=1:2	2.04	27.78	2.583
Average	2.04	28.335	2.537
dhtz:BDC=1:3	1.13	29.9	2.58
dhtz:BDC=1:3	1.14	29.79	2.655
Average	1.135	29.845	2.6175