Electronic Supplementary Information

Time Modulation of Defects in UiO-66 and Application in Oxidative

Desulfurization

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Chemicals

All the reagents such as zirconium(IV) chloride, benzene-1,4-dicarboxylic acid, N, N-dimethylformamide (DMF), dibenzothiophene (DBT), acetonitrile, H₂O₂ (30%) and n-octane were used as received without further purification.

Synthesis of defective UiO-66

1.80 g of zirconium chloride was dissolved in 20 mL DMF and stirred for 30 min. In another beaker, 1.27 g of terephthalic acid was dissolved in 20 mL DMF stirred for 15 min, 0.65 mL ammonia aqueous (2 mol L⁻¹) was then added. The terephthalic acid solution was slowly added to the dissolved zirconium chloride. After this, 60 mL DMF was added to the above solution. The mixture was moved into 250 mL threenecked flask and stirred at 110 °C for demanded time (t h). The final products were separated by centrifugation, washed three times with methanol and dried at 80 °C. The obtained products were named as UiO-66-t (t = 0.5h, 1h, 3h, 5h, 10h, 15h, 20h).

Synthesis of UiO-66-S

0.24 g of zirconium chloride and 0.17 g of terephthalic acid were dissolved in 60 mL DMF, then 0.19 mL deionized water was added and stirred at room temperature

for 10 min. After this, the above mixture was transferred to 100 mL Teflon liner stainless steel autoclave and placed in an oven at 120 °C for 24 h. The final product was separated by centrifugation, washed three times with methanol and dried at 80 °C. The obtained product was named as UiO-66-S.

Catalytic activity tests (oxidation of DBT)

The oxidation of DBT was carried out on a closed vessel at 60 °C using the UiO-66-t as catalyst. In a typical experiment, the catalyst (5 mg) was added to 2 mL acetonitrile containing DBT (1000 ppm of sulfur), then 0.05 mL of H_2O_2 aqueous (30%) was added. The DBT content was monitored at fixed time intervals by GC-MS.

The oxidative desulfurization was also performed in a model diesel. In a typical experiment, 50 mg of UiO-66-1h was added to the mixture of 20 mL n-octane containing DBT (1000 ppm of sulfur) and 20 mL acetonitrile, and the resulting mixture was stirred for 10 min. The catalytic step of the process is initiated by the addition of 0.05 mL H_2O_2 aqueous (30%). The sulfur content was periodically quantified by GC-MS analysis using n-dodecane as a standard. In the recycling experiment, the UiO-66-1h was recovered by centrifugation after 1 h oxidation reaction, washed with massive methanol, dried at 80 °C, and subjected to another cycle.

GC-MS analysis was carried on an Agilent 7890B-5977A MS with HP-5MS column (30 m \times 0.25 mm \times 25 μ m). The temperature of the column was held at 100 °C for 2 min, then increased to 280 °C at a ramp rate of 10 °C min⁻¹ and held at 280 °C for 1 min. The GC injector temperature was set to 250 °C and the carried gas (He)

was set to a constant flow rate of 1 mL min⁻¹.

Characterization

Powder X-rays diffraction (XRD) was collected on a Puxi XD-3 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm, 40 kV/30 mA) at the scanning step of 2 °/min in the 20 range from 5 to 45°. Raman spectra were recorded on a Renishaw inVia Raman microscope spectrometer. A diode laser emitting 532 nm was used; photons scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and were simultaneously collected on a CCD camera; the collection optic was set at 20X objective. Raman spectrum was collected in range of 3000-100 cm⁻¹. The spectra were collected at 1% Laser power with 100 acquisitions of 20 seconds each. Scanning electron microscope (SEM) images of the catalysts were performed on a JEOL JSM-6701F field emission scanning electron microscope. TGA-DSC was recorded on a Mettler Toledo TGA-DSC3⁺ instrument with a heating rate of 10 °C min⁻¹ from room temperature to 700 °C in an air flow of 20 mL min⁻¹. N₂ adsorption-desorption isotherms were analyzed out on a Micrometrics ASAP 2020 instrument analyzer at 77 K. Prior to analysis, all samples were activated on a Micrometrics Smart VacPrep System at 200 °C for 12 hours. A minimum of 50 mg was used for each analysis. The surface areas were calculated by the multi-point BET (Brunauer-Emmett-Teller) method, and the total pore volumes were estimated from the adsorbed amount at a relative pressure P/P₀ of 0.99. Micropore surface area and micropore volume were calculated from t-plot equation. Pore size distribution was derived from the nonlocal density functional theory model. NH₃-TPD measurements were performed on a Huasi DAS-7000 adsorption instrument. 40 mg of catalyst was charged into a quartz tube, and then pretreated at 300 °C for 4 h under Ar. Then the catalyst was cooled to 50 °C, saturated with dried NH₃ and blown with Ar to remove the physical adsorbed NH₃. The desorption process was recorded from 50 to 350 °C at a heating rate of 5 °C/min by a thermal conductivity detector.



Fig. S1 The FWHM (solid line, left axis) of selected diffraction peaks of UiO-66 with different synthesis time and XRD pattern (dotted line, right axis) of UiO-66-20h.



Fig. S2 SEM images of UiO-66 samples.

 Table S1 The average particle sizes of UiO-66-t samples obtained by the SEM images.



Fig. S3 N_2 adsorption-desorption isotherms (77 K) of UiO-66 with different synthesis time. For clarity, the isotherms of 10 h, 15 h and 20 h are offset along the y axis by 200, 400 and 550 cm³ g⁻¹, respectively.



Fig. S4 Pore size distributions of UiO-66 with different synthesis time by the nonlocal density functional theory model.

Sample	$S_{BET}{}^{(a)}(m^2 g^{-1})$	Micropore area ^(b) $(m^2 g^{-1})$	Total pore volume $^{(c)}(cm^3 g^{-1})$
UiO-66-0.5h	1052	362	1.415
UiO-66-1h	1192	450	1.574
UiO-66-3h	1050	525	1.399
UiO-66-5h	1145	761	0.8129
UiO-66-10h	1086	743	0.7538
UiO-66-15h	1153	854	0.5384
UiO-66-20h	1340	1035	0.6077

Table S2 Textual properties of UiO-66-t samples.

^{a)} Specific surface area calculated using the BET equation; ^{b)}micropore surface area calculated from t-plot equation; ^{c)} single point pore volume calculated at relative pressure of 0.99.



Fig. S5 NH₃-TPD profiles of UiO-66-0.5h and UiO-66-15h. The peak area ratio of UiO-66-0.5h to UiO-66-15h is 1.06:1, respectively.



Fig. S6 Raman spectra of UiO-66 with different synthesis time.





As evaluated by the TGA, the apparent linker-missing defects in UiO-66-S and UiO-66-5h are 15% and 38%, respectively.



Fig. S8 Catalytic activities of UiO-66-S and UiO-66-5h. Catalyst: 5 mg; H₂O₂: 0.05 mL; temperature: 60 °C; DBT in acetonitrile: 2 mL (1000 ppm of sulfur).



Fig. S9 The XRD patterns (a) and N_2 adsorption-desorption isotherms at 77 K (b) of fresh and recovered UiO-66-1h.



Fig. S10 The XRD patterns of UiO-66-S and UiO-66-5h.