

Electronic Supplementary Information (ESI)

Enhanced adsorptive desulfurization with flexible metal-organic frameworks in the presence of diethylether and water

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Experimental:

Materials: Trimesic acid (H_3BTC , $C_9H_6O_6$, 98%), terephthalic acid (TPA, $C_6H_4-1,4-(CO_2H)_2$, 98%), chromium chloride ($CrCl_3 \cdot 6H_2O$, 96%), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, 99%), *n*-octane (C_8H_{18} , 99%), benzothiophene (BT, C_8H_6S , 98%), dibenzothiophene (DBT, $C_{12}H_8S$, 98%), and thiophene (Th, C_4H_4S , 99%) were purchased from Sigma Aldrich Co. Dimethyldibenzothiophene (DMDBT, $C_{14}H_{12}S$, 97%) and trimethyl 1,3,5-benzenetricarboxylate (Me_3-BTC , $C_{12}H_{12}O_6$, 98%) were obtained from Alfa Aesar. Diethylether ($C_2H_5OC_2H_5$, 99.0%) was obtained from OCI Chemicals. Toluene (C_7H_8 , 99%) and *N,N*-dimethylformamide (DMF, C_3H_7NO , 99%) were purchased from Duksan pure chemicals Co. Chromium (VI) oxide (CrO_3 , 98%) and nitric acid (HNO_3 , 60%) were obtained from Junsei chemicals.

Synthesis of MIL-53s: MIL-53(Al) and MIL-53(Cr) used in this study were synthesized hydrothermally under autogeneous pressure.¹ Microwaves (Mars-5, CEM) were used as a heating source in order to take advantage of rapid synthesis of porous materials under microwave irradiation. For the synthesis of MIL-53(Al), aluminum chloride hexahydrate, terephthalic acid and deionized water were mixed in the molar ratio of 1Al:0.5TPA:80H₂O. The reaction mixtures containing TPA, aluminum chlorides and water were stirred for 5 min, loaded into a Teflon-lined autoclave, sealed and placed in the microwave oven and finally heated for 2.5 h at 200 °C under autogeneous pressure. The MIL-53(Cr) was synthesized similarly from chromium (III) chloride hexahydrate. The reaction temperature and time were changed a bit for the syntheses of MIL-53(Cr) (210 °C, 2 h). After the synthesis, the MOF samples were recovered by cooling, filtration, water washing and drying. To remove TPA from the as-synthesized MOFs, purification was carried out with

sonication using an ultrasonic generator (VC×750, max. power 750 W, Sonic & materials, Inc.) in the presence of DMF following the reported purification method. Briefly, 0.3 g of a MOF such as MIL-53(Al) was suspended in 20 ml of DMF and sonicated for 1 h at 70 °C. The purified MOFs were collected after filtration and dried at 150 °C for 5 h and stored in a desiccator. Hydration of the adsorbents was done by exposing the MOFs (kept in petri dish) in open air for 48 h.

Synthesis of MIL-100s: MIL-100(Al) was synthesized from aluminum nitrate nonahydrate, Me₃-BTC, sodium hydroxide (NaOH, 4 M), nitric acid and deionized water similar to the reported methods² under autogenous pressure at 210 °C. The reactant composition was Al(NO₃)₃·9H₂O : 0.67 Me₃-BTC : 255 H₂O : 1.26 HNO₃. For conventional electric crystallization, the reaction mixture of 20 g was loaded in a Teflon-lined autoclave and put in a preheated electric oven. The crystallization time was 2 h. MIL-100(Cr) was synthesized similar to the reported method.³ For the preparation of MIL-100(Cr); chromium (VI) oxide, HF, H₃BTC and H₂O were mixed with a molar ratio of CrO₃ : HF: 0.67 H₃BTC : 265 H₂O. The reactant mixture was then transferred to a Teflon-lined autoclave and heated in a conventional electric oven for 4 days at a temperature of 220 °C. After the crystallization for a fixed time, the autoclaves of synthesized MOFs were cooled to room temperature and solid products was recovered by filtration. The solid products were washed with a water/ethanol mixture (1:1 v/v) and stirred in ethanol at 60 °C for 5 h to remove the unreacted organic linkers. The purified MOFs, after filtration, were dried overnight at 100 °C.

Synthesis of MIL-68(Al): MIL-68(Al) was synthesized similar to the reported method.⁴ TPA (5.0 g) and aluminum chloride hexahydrate (4.88 g) were dissolved in 300 mL

of DMF. The mixture was placed in a round bottom flask equipped with a condenser under stirring, and heated for 18.5 h at 130 °C under air. After cooling solid product was recovered by filtration, and, dispersed at room temperature in 3×50 mL DMF under stirring for the removal of the free TPA. Finally, in order to further remove the DMF embedded in the pores, the same procedure was repeated four times instead of the 4×50 mL methanol. The purified MOF, after filtration, was dried overnight at 100 °C.

Characterization: The crystal phase of the samples was determined with an X-ray diffractometer (D2 Phaser, Bruker, CuK α radiation). Nitrogen adsorption isotherms were acquired at –196 °C using a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation of the adsorbents at 150 °C for 12 h. The BET surface area and total pore volumes were evaluated with the BET equation and adsorbed amount ($P/P_0=0.99$), respectively.

Adsorption experiments: A stock solution of Th, BT, DBT or DMDBT (10,000 ppm) was prepared by dissolving those in *n*-octane. Solutions with different concentrations (5000 – 50 ppm) were prepared by successive dilution of the stock solutions. Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C and were kept in a desiccator. The adsorbents were added to SCC solutions with fixed concentrations. The solutions containing the adsorbents were mixed well *via* magnetic stirring and maintained for a fixed period of time (1 h to 12 h) at a constant temperature of 25 °C. After adsorption for a pre-determined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5 μ m), and the concentration of the SCC was measured using a gas chromatograph (DS

Science, IGC 7200) equipped with a flame ionization detector. The maximum adsorption capacity (Q_0) was obtained using the Langmuir equation.

Calculation of adsorption capacity (q_t): All the adsorption capacities (mg/g) were calculated from the difference between final and initial concentrations of an adsorbate by using following equation:

$$q_t = \frac{(C_i - C_f)V}{m}$$

Where,

q_t = adsorbed amount in time t (mg/g)

C_i = initial concentration of the adsorbate (mg/ml)

C_f = final concentration after adsorption (mg/ml)

V = volume of the solution subjected to a single adsorption (ml)

m = mass of the adsorbent taken during a single adsorption (g)

Calculation of maximum adsorption capacity (Q_0): The maximum adsorption capacity (Q_0) was calculated using the Langmuir adsorption isotherm. The adsorption isotherms for different adsorbents were plotted according to the Langmuir equation^{5,6}

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b}$$

Where,

C_e : the equilibrium concentration of the adsorbate (mg/L)

q_e : the amount adsorbed at equilibrium (mg/g)

Q_0 : the Langmuir constant (maximum adsorption capacity, mg/g)

b : the Langmuir constant (L/mg)

Therefore, the maximum adsorption capacity, Q_0 , could be obtained from the reciprocal of the slope of a plot of C_e/q_e against C_e .

FTIR experiments: The FTIR spectra were obtained at 30 °C with Thermo Nicolet 6700 spectrometer in a high temperature reaction chamber (Harrick HVC-DRP) in diffuse reflectance mode. MIL-53(Al) was evacuated for 2 h at 300 °C under helium (20 cc/min) flow, and Th and DEE were adsorbed on dehydrated MIL-53(Al) by flowing a gas mixture of Th (1 cc/min) and DEE (4 cc/min) in helium (15 cc/min).

References:

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Table S1: Textural properties of the MOFs applied in this study.

MOFs	S_{BET} , m^2/g	PV_{tot} , cm^3/g	PV_{mic} , cm^3/g
MIL-53(Al)	1282	0.47	0.45
MIL-53(Cr)	1301	0.51	0.49
MIL-100(Al)	1486	0.70	0.38
MIL-100(Cr)	1576	0.76	0.40
MIL-68(Al)	1119	0.65	0.39

Table S2. Maximum adsorption capacities (Q_0) for the adsorption of DBT and DMDBT over MIL-53(Al) MOFs.

Adsorbent	Solvent	Q_0 , mg-DBT/g	Q_0 , mg-DMDBT/g
MIL-53(Al)	<i>n</i> -octane	401	211
MIL-53(Al)	<i>n</i> -octane+ 5% DEE	520	
MIL-53(Al)- Hydrated	<i>n</i> -octane		277

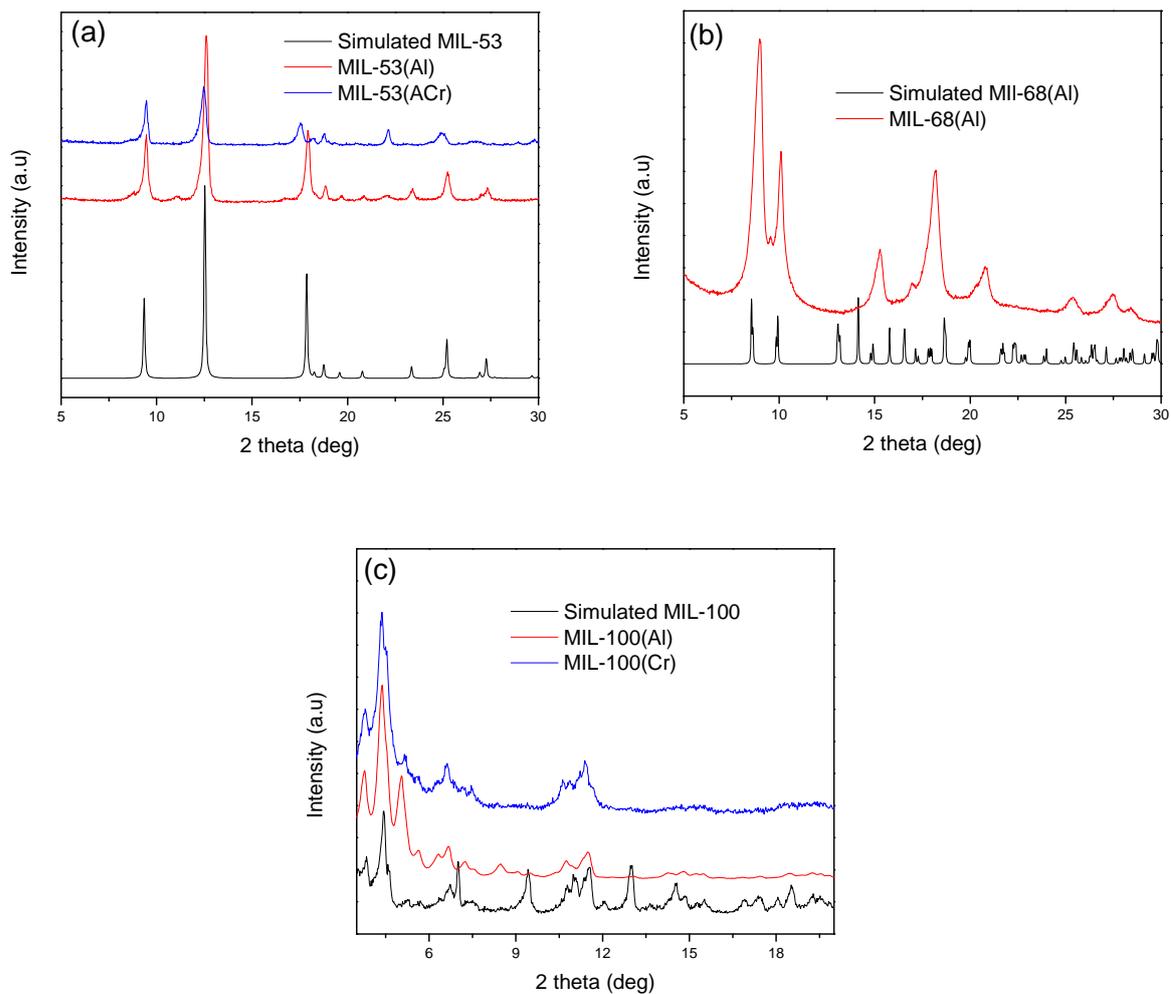


Fig. S1. XRD patterns of (a) MIL-53s, (b) MIL-68(Al) and (c) MIL-100s.

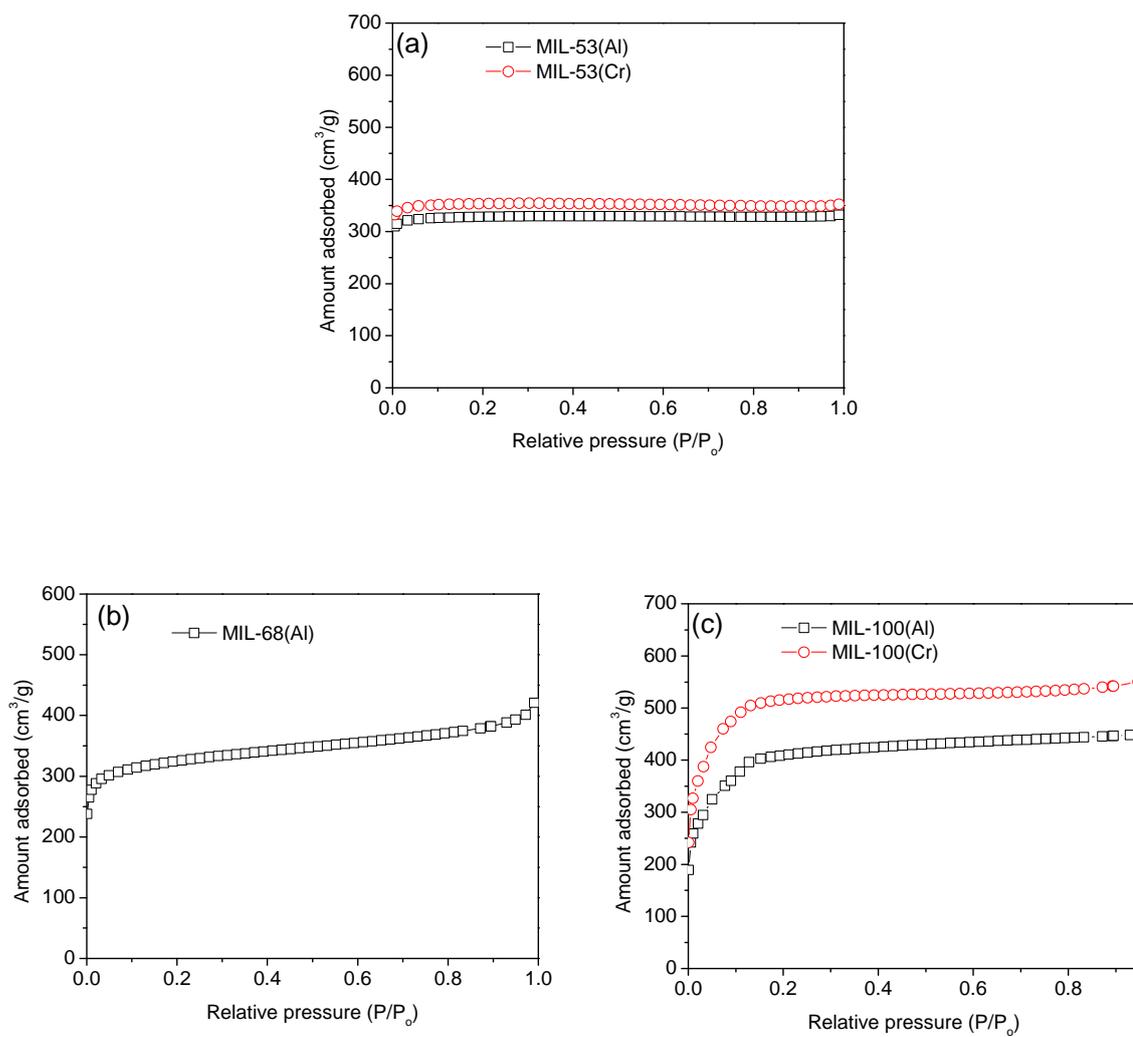


Fig. S2. N₂ adsorption isotherms of (a) MIL-53s, (b) MIL-68(Al) and (c) MIL-100s.

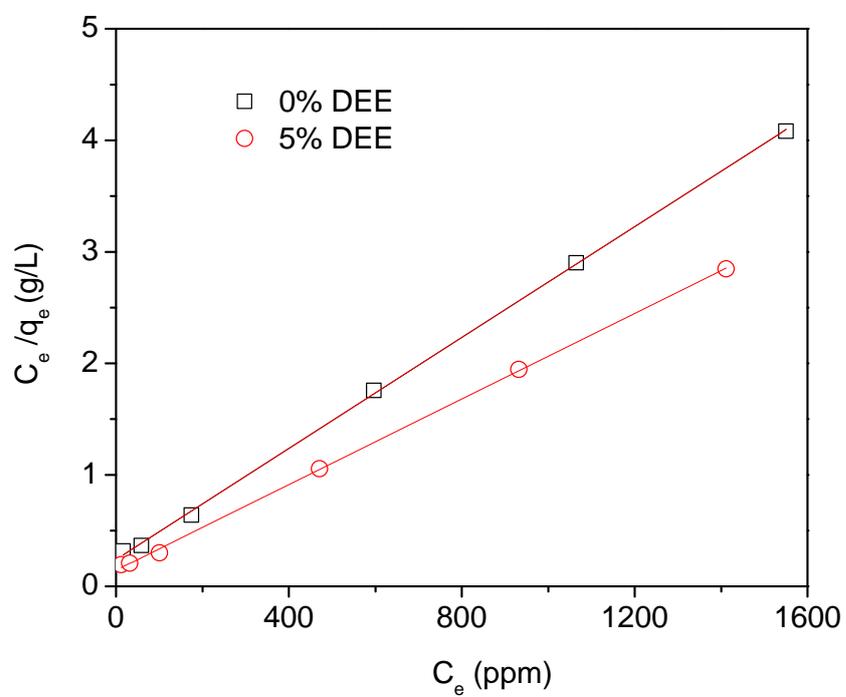


Fig. S3. Langmuir plots for the adsorption of DBT over MIL-53(Al) (from *n*-octane or *n*-octane/DEE solvent).

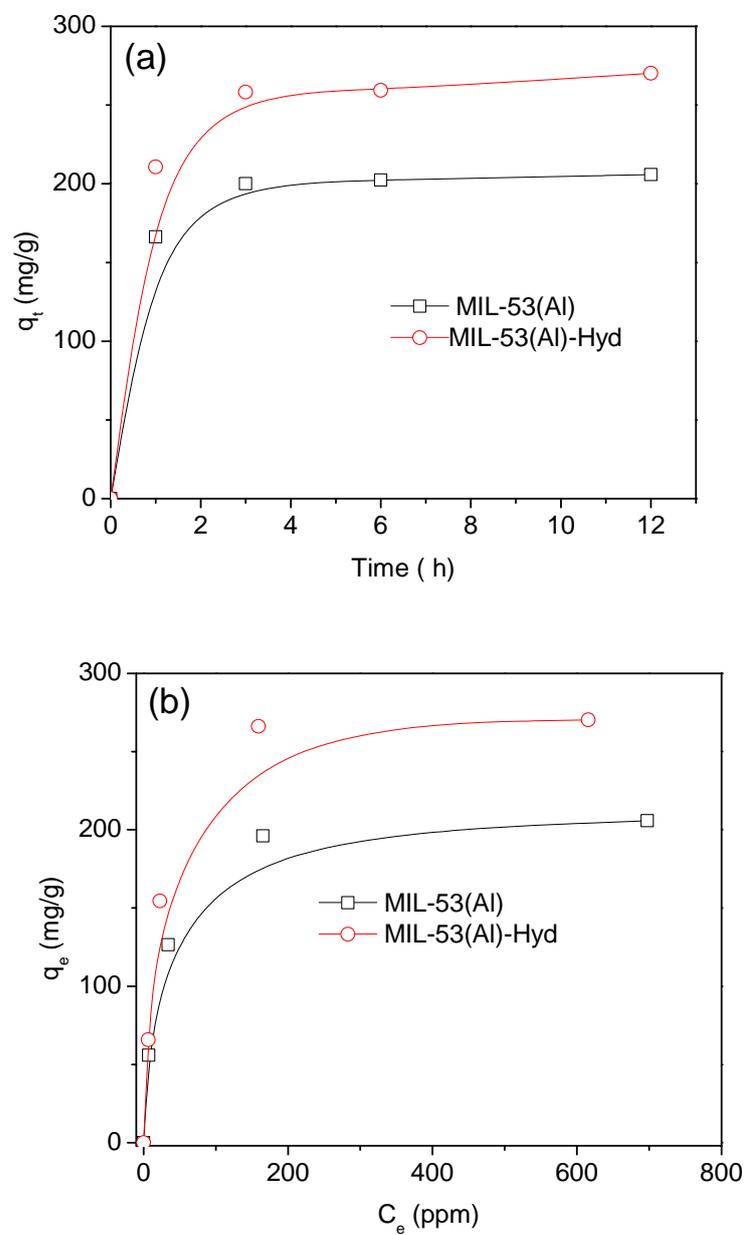


Fig. S4. (a) Effect of contact time on the adsorbed amount of DMDBT (initial concentration was 1000 ppm) over MIL-53(Al) MOFs. (b) Adsorption isotherms of the MIL-53(Al) MOFs for the DMDBT adsorption. In both cases, solvent was n-octane (0% DEE) and the MIL-53(Al) was dehydrated or hydrated before adsorption.

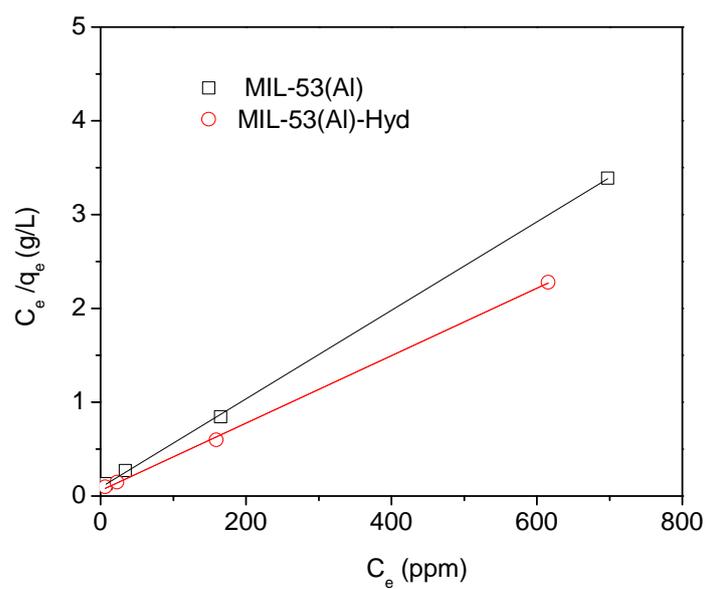


Fig. S5. Langmuir plots for the adsorption of DMDBT over dehydrated or hydrated MIL-53(Al) (from *n*-octane solvent).

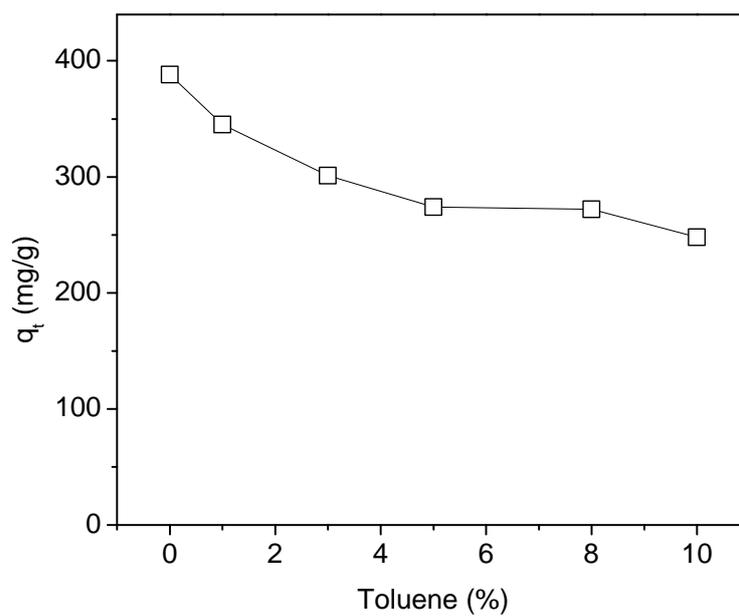


Fig. S6. Effect of toluene content (as additive to *n*-octane solvent) on the adsorbed amount of DBT over MIL-53(Al). The initial DBT concentration was 1000 ppm and the adsorption time was 12 h.

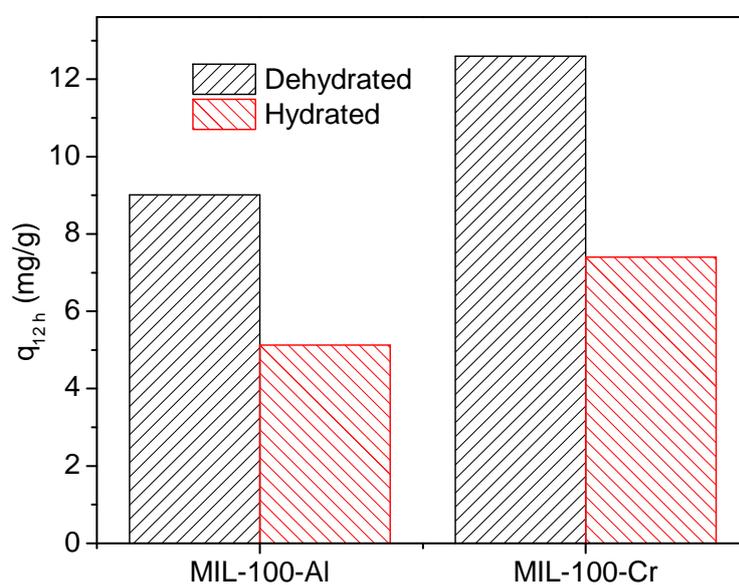


Fig. S7. Adsorbed amount of BT over MIL-100(Al) and MIL-100(Cr). The MOFs were dehydrated or hydrated before adsorptions. The initial BT concentration was 500 ppm and the adsorption time was 12 h.

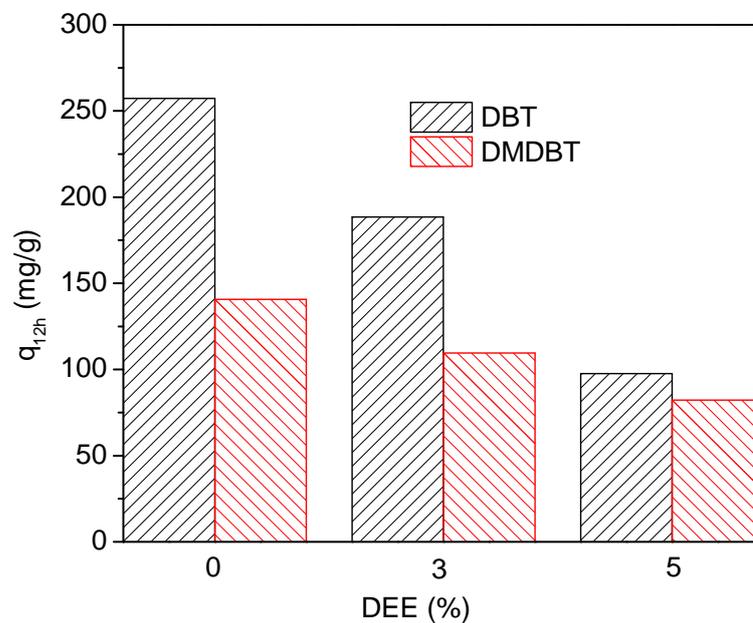


Fig. S8. Effect of DEE content in n-octane solvent on the adsorbed amount of DBT and DMDBT over MIL-68(Al). The initial DBT or DMDBT concentration was 1000 ppm and the adsorption time was 12 h.

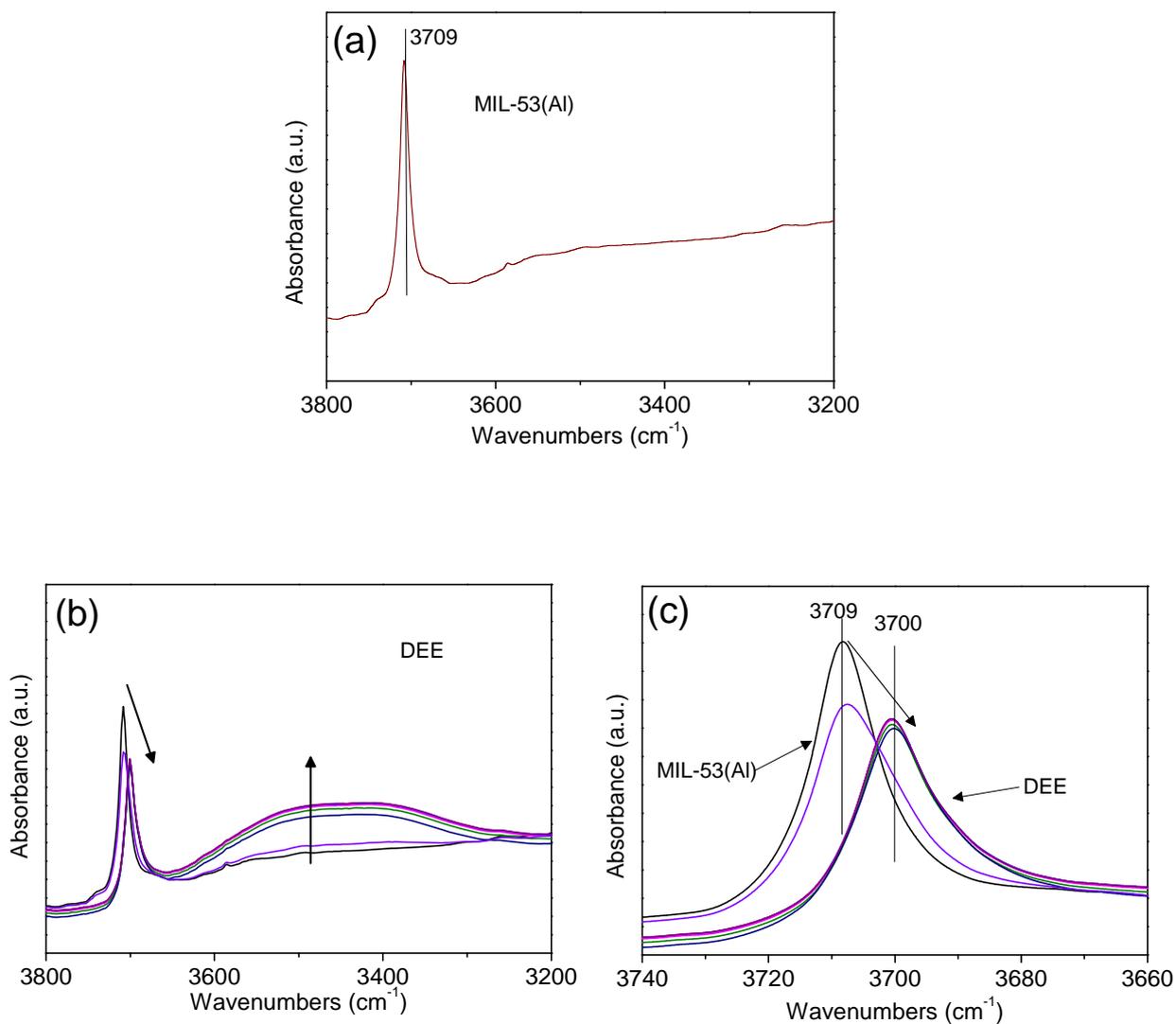


Fig. S9. FTIR spectra of (a) dehydrated MIL-53(Al), (b) MIL-53(Al) with the adsorption of DEE and (c) The enlarged spectra of (b). Arrows show the direction of spectra change with adsorption time.

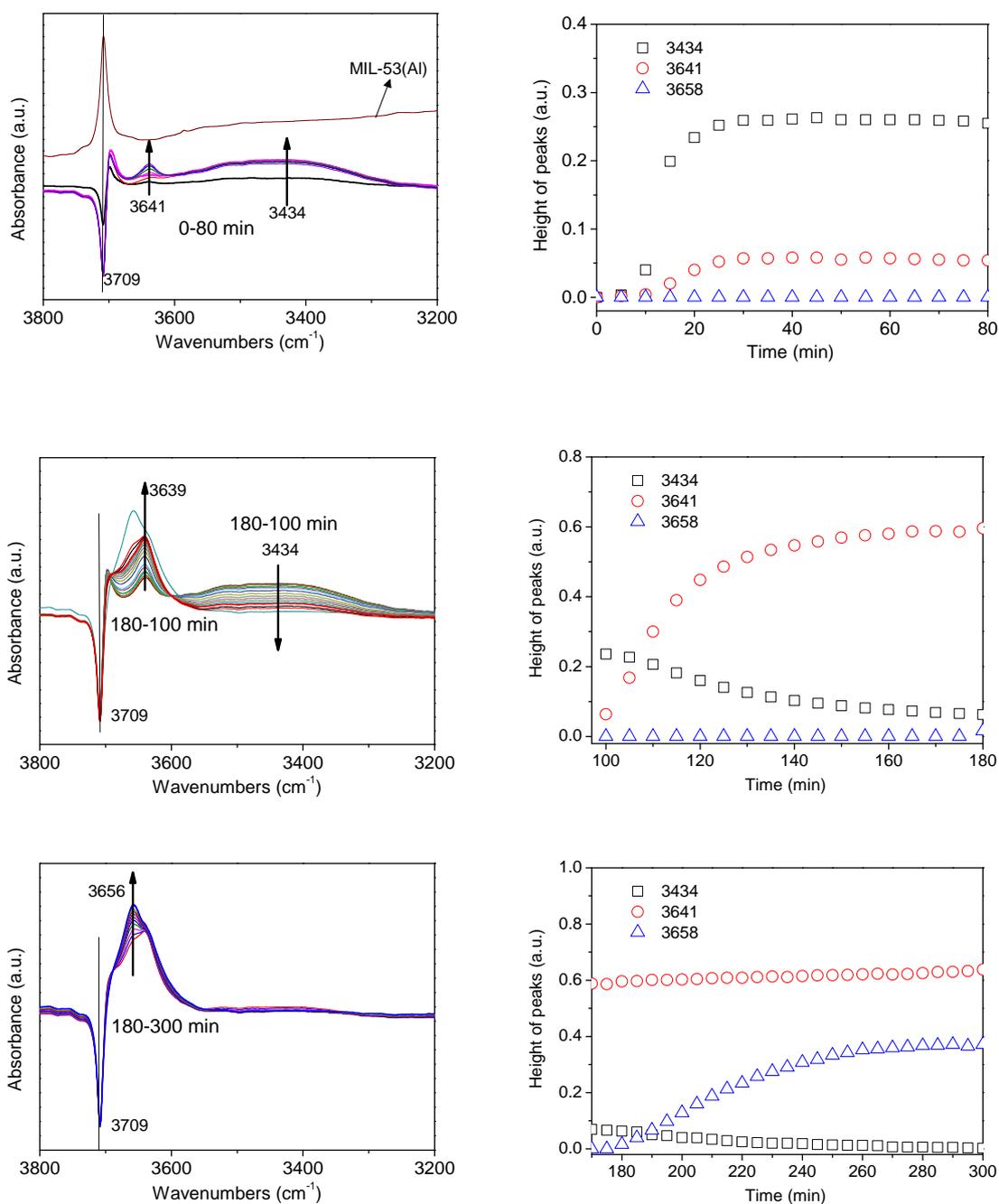


Fig. S10. The detailed changes of FTIR spectra with adsorption time after adsorption of Th/DEE. Adsorption times are shown in each figure. Right hand graphs show the peak height of three bands with adsorption time.