ELECTRONIC SUPPLEMENTARY INFORMATION

High and reversible H₂S capture by an Al(III)-based MOF

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1. Crystal Structure of MIL-53(Al)-TDC

The crystal structure of MIL-53(Al)-TDC (Fig. S1) was constructed form the cell parameters and atomic positions reported by Stock *et al.*¹ (*Pmna*, a = 14.628 Å, b = 6.557 Å and c = 14.725). Channel dimensions were estimated using the van der Waals radii of the atoms using the software CrystalMaker.²



Fig. S1. (top) view of the crystal structure of MIL-53(Al)-TDC along *b* axis showing 8.9 x 9.2 Å channels; (bottom) binuclear building block of two Al(III) metal ions oxygen-octahedra bridged by a μ_2 -hydroxo group, and the TDC²⁻ ligand, through <101>.

2. Experimental

Synthesis of MIL-53(Al)-TDC

The synthesis of MIL-53(Al)-TDC ([Al(OH)TDC]; TDC = 2,5-thiophenedicarboxylate) was based on a method previously reported by Stock *et al.*,¹ an modified as follows: 64 mg of AlCl₃ (Reagent Plus Sigma Aldrich, 99%) and 62 mg of 2,5-thiophenedicarboxilic acid were mixed in 1.8 mL of DMF and 2.5 mL of H₂O. This mixture was heated up to 100 °C for 5 hours in a pressure tube of 20 mL. After the reaction was completed and cooled down to room temperature, the product was filtered off under vacuum and washed with DMF (5 mL), to remove the excess of ligand inside the MOF material. The as-synthesised product was then mixed with DMF and heated to 150 °C for 1 h. To remove DMF molecules from its pores, samples of DMF treated MIL-53(Al)-TDC, were acetone-exchanged for 3 days.

Elemental Analysis

<u>Activated sample of MIL-53(Al)-TDC</u>: Elemental analysis (% calc/found), [Al(OH)TDC] = $[Al(\mu-OH)(C_6H_2O_4S); (C 33.6/33.2, H 1.4/1.3, S 14.9/15.1).$

<u>Sample of MIL-53(AL)-TDC after a H₂S adsorption experiment:</u> Elemental analysis based on the activated MIL-53(Al)-TDC (% calc/found), $[Al(OH)TDC] = [Al(\mu-OH)(C_6H_2O_4S);$ (C 33.6/34.0, H 1.4/1.4, S 14.9/14.8).

Adsorption isotherms for N₂

N₂ isotherms (up to 1 bar and 77 K) was recorded on a Belsorp mini II analyser under high vacuum in a clean system (sealed chamber inside the adsorption instrument, were the gas dossing takes place, which is kept 'clean' by avoiding the samples to flow into the system by using adequate cell filters) with a diaphragm pumping system. Then, an acetone-exchanged sample of MIL-53(Al)-TDC was activated at 200 °C for 4 hours under vacuum (~3 x 10⁻⁴ bar) and a N₂ adsorption isotherm was measured at 77 K to estimate its BET surface area ($0.01 < P/P_0 < 0.04$), which was equal to approximately 1400 m² g⁻¹. The obtained surface area is higher than the reported value (1150 m² g⁻¹),¹ also the N₂ isotherm shows a type-I shape with a type H3 hysteresis loop, which can be associated to some inter-particle capillary condensation.



Fig. S2. N2 adsorption isotherm at 77 K for MIL-53(Al)-TDC (left) and micropore distribution (right).

Thermogravimetric analysis (TGA)

TGA were performed in a TA Instruments Thermoblance, Q500 HR under N_2 atmosphere using the High-Resolution mode (dynamic rate TGA) with a maximum rate of 5 K min⁻¹ (sensitivity 1, res. 5), from room temperature to 800 °C. Hi-Res technique was used to improve the transition resolution.³



Fig. S3. TGA curves for MIL-53(Al)-TDC synthesised sample (purple) and activated sample (green).

Scanning electron microscopy images (SEM)

SEM were recorded using a JEOL Benchtop Scanning Electron Microscope, Neoscope JCM-6000 using secondary electrons at 15 kV current in high vacuum.

PXRD experiments

Powder X-ray diffraction (PXRD) patterns were collected in Bragg-Brentano geometry with Cu-K α l radiation ($\lambda = 1.540562$ Å) in a Rigaku ULTIMA IV with a nickel filter. The powder patterns were recorded from 5 to 50° (2 θ) in 0.01° steps and a scan rate of 0.319° min⁻¹. The PXRD pattern of the as-synthesised sample showed a good match with the reported pattern (see Fig. S7).

H₂S adsorption experiments

Dynamic breakthrough experiments were carried out in a home-made system (Scheme S1). The adsorption column was made from quartz glass with an internal diameter of 7 mm, with a porous glass bed to hold the sample. The adsorption column was covered with a temperature-controlled heating jacket. The column downstream was monitored with a gas chromatograph (HP-5890) equipped with a HP-PLOT 1 column and a thermal conductivity detector (TCD). The GC is equipped with an automatic injection valve.

Acetone exchanged samples of MIL-53(Al)-TDC were activated *in situ* at 200 °C for 4 hour with a constant flow of dry N_2 and then slowly cooled to 30 °C. Then the H_2S concentration was adjusted with a mass flow controller fed with two lines: dry N_2 and H_2S/N_2 15 %vol (Scheme S1). The breakthrough experiments were carried out at 30 °C and the downstream flow was analysed with a GC, the complete breakthrough of H_2S was indicated by the downstream gas concentration reaching the initial feed. The reactivation of the sample was at 200 °C for 2 hours under a flow of dry N_2 gas.



Scheme S1. Breakthrough dynamic system for H₂S uptake experiments.

The H₃S adsorption capacity was calculated using Eq. S1, where $V_{\mu\nu\nu}$ represents the H₃S volumetric capacity (cm³ g³), '*m*' the adsorbent mass (g), '*F*' the input flow rate (cm³ min³), '*C*_t' and '*C*_t' the influent and downstream H₃S concentrations respectively (% vol), and '*t*' the time (min).⁴

$$V_{H_2S} = \frac{F}{C_f \cdot m} \cdot \int_0^t (C_f - C_t) dt$$
 Eq. S1

As mentioned before, the adsorption column has a porous glass bed thus, a blank run before each experiment was measured to eliminate the adsorption contribution of the column. In Fig. S4 the blue circles represent the adsorption of the column, and the black circles represent the MOF adsorption. Then the MIL-53(Al)-TDC corrected volumetric capacity V_{mesorr} was estimated using Eq. S2.

$$V_{H_2S,corr} = V_{H_2S,blank} - V_{H_2S,sample}$$
 Eq. S2

The H_aS adsorption capacity is often reported as ' $q_{\mu\nu\sigma}$ ' (mol g⁴), this value was roughly estimated with the volumetric adsorption capacity ' $V_{\mu\nu\sigma\sigma}$ ' (cm³ g⁴) and the ideal gas law Eq. S3. Where 'p' is the system pressure (77.3 kPa), 'T' the measurement temperature (303 K), and 'R' the ideal gas constant (8314.4598 cm³ kPa K⁴ mol⁴).

$$q_{H_2S} = \frac{V_{H_2S,corr} \cdot p}{R \cdot T}$$
 Eq. S3



Fig. S4. Breakthrough curves for MIL-53(Al)-TDC and the blank.

 Table S1. H₂S uptake (breakthrough system).

Al-MIL-53-TDC weight	49.3 mg
Blank area	48.1478 %v min
MIL-53(Al)-TDC area	44.3792%v min
Blank area – MOF area	3.7686 %v min
H ₂ S ads.	22.6116 mL
H ₂ S ads.	0.8942 mmol
H ₂ S ads.	30 mg
H ₂ S adsorption	616.71 mg/g
H ₂ S adsorption	18.13 mmol/g

Gravimetric H₂S adsorption (kinetic system). H₂S was generated *in situ*, in an isolated system inside a dry box, by mixing $HCl_{(aq)}$ and Fe_2S_3 as shown in Fig, S5. Then generated H₂S passed through a water trap (CaCl₂). Finally, the H₂S reached to the saturation chamber, where activated (200 °C, 4 h and under vacuum) samples of MIL-53(Al)-TDC adsorbed H₂S. The H₂S adsorption was monitored gravimetrically (with a digital balance placed inside the dry box), as function of time to finally reach saturation (18.1 mmol g⁻¹see Fig. S5).



Fig. S5. Gravimetric H₂S adsorption placed inside a dry box.



Fig. S6. Gravimetric H₂S adsorption for MIL-53(Al)-TDC.

DRIFT Spectroscopy

DRIFT spectra of the MOF material (MIL-53(Al)-TDC) were measured (*in-situ* and at 30 °C) using an FTIR Nicolet 6700-spectrophotometer (DTGS detector) with a 4 cm⁻¹ resolution equipped with a diffuse reflectance vacuum chamber with CaF₂ windows. DRIFT spectra were collected on an activated MIL-53(Al)-TDC sample (~8 x 10⁻⁶ bar and 200 °C for 4 hours), and after H₂S adsorption (under an atmosphere of H₂S).

3. PXRD, SEM, TGA and N₂ adsorption experiments after H₂S



Fig. S7. Reported PXRD pattern for MIL-53(Al)-TDC (black), the as-synthesised (experimental) pattern (red) and the pattern of MIL-53(Al)-TDC after H_2S (blue).



Fig. S8. Reported PXRD pattern for MIL-53(Al)-TDC (black), the as-synthesised (experimental) pattern (red) and the pattern of MIL-53(Al)-TDC after five cycles of H_2S (green).



Fig. S9. MIL-53(Al)-TDC SEM images before (left) and after H₂S adsorption (right).



Fig. S10. TGA for MIL-53(Al)-TDC after H₂S experiments.



Fig. S11. N₂ adsorption isotherm at 77 K for MIL-53(Al)-TDC as-synthesised (blue) and after H₂S experiments (red). The BET surface area estimated for MIL-53(Al)-TDC was of approximately 1396 $m^2 g^{-1}$.

4. H₂S breakthrough experiments on known MOF materials

Our home-made breakthrough system was tested with other reported MOF materials (Fig. S12): MOF- 74(Zn), HKUST-1 and MIL-101(Cr).² 50 mg of each sample were activated *in situ* at 180 °C for 1 hour with a constant flow of dry N₂ and then slowly cooled to 30 °C. Then the H₂S concentration was adjusted to 6 %vol. Adsorption capacity at 6 %vol of H₂S concentration for the reported materials are correspondent with the reported values (Table S2).



Fig. S12. H₂S adsorption breakthrough curves at 30 °C for Mg-CUK-1, MOF-74(Zn), HKUST-1 and MIL-101(Cr). Measurements using 6 %vol. H₂S/N₂ feed concentration and a 30 cm³ min⁻¹ flow rate.

Table	S2.	H_2S	adsor	ption	capaci	ty for	knowr	1 MOF	materials.	Breaktl	hrough	measure	ments	using (5
%vol.	H_2S	$/N_2$ f	feed co	oncen	tration	and a	30 cm	3 min^{-1}	flow rate.						

Matarial	H ₂ S uptake (mmol g ⁻¹)			
wrateriai	This work	Reported ^{5,11c}		
Mg-CUK-1	1.39	1.41		
MOF-74(Zn)	1.72	1.64		
HKUST-1	1.04	1.1		
MIL-101(Cr)	0.52	0.4		

5. H₂S desorption by Hi-Res TGA



Fig. S13. Hi-Res TGA of a H₂S saturated MIL-53(Al)-TDC sample. Left axis represents the scale as obtained from the instrument, and right axis represents the corrected scale used to determine the adsorbed H₂S (assuming the H₂S is desorbed at 65 °C). Inset shows the desorption of H₂S at low temperatures (scale set to zero when H₂S is completely desorbed).

6. in situ DRIFT experiments



Fig. S14. DRIFT spectra at 30 °C of MIL-53(Al)-TDC after H_2S adsorption, emphasising the v(S-H) absorption band.



Fig. S15. DRIFT spectra at 30 °C of MIL-53(Al)-TDC after H_2S adsorption, emphasising the v(C-S) absorption band.



Fig. S16. DRIFT spectra at 30 °C of MIL-53(Al)-TDC (blue), MIL-53(Al)-TDC with H_2S (green) and MIL-53(Al)-TDC after H_2S adsorption (red).

7. Monte Carlo Simulations

Microscopic models for MOF and H₂S and Interatomic Potentials

The initial atomic coordinates for MIL-53(Al)-TDC were taken from a previous study reported by Stock *et al.*¹. The Lennard-Jones (LJ) parameters for the organic and inorganic parts of the MIL-53(Al)-TDC were taken from UFF⁶ and DREIDING⁷ force fields respectively. The partial atomic charges for each framework atom of MIL-53(Al)-TDC were extracted from periodic Density Functional Theory (DFT) calculations using the ESP method as implemented in Dmol³. We considered the functional PBE⁸ and DNP⁹ as basis set. The H₂S molecule was represented by the model reported by Kamath *et. al.*¹⁰ This corresponds to a rigid model with three charged sites centered in the atomic positions where only the S atom is a a LJ interacting site, with a S-H bond of 1.34 Å and a H-S-H bond angle of 92.5°. The MIL-53(Al)-TDC/H₂S interactions were described using a 12-6 LJ potential and a coulombic contribution. Using a general approach adopted in previous studies,¹¹ the H atom from the μ_2 -OH group and the Al atoms interacts with the guest molecules only through electrostatic interactions. LJ crossed parameters between the MOF material and the guest molecules were calculated with the Lorentz-Berthelot mixing rules. A cut off distance of 12 Å was used for the LJ contributions, while the long-range electrostatic interactions were handled with the Ewald summation technique.¹²



Fig. S17. Labels of the atoms for the inorganic and organic parts of MIL-53(Al)-TDC.

Atom Type	ε (K)	σ (Å)
Al	0	4.0081
S	137.88	3.5948
C1	47.856	3.4729
C2	47.856	3.4729
C3	46.856	3.4729
01	48.158	3.0331
O2	30.193	3.1181
H1	7.6489	2.8464
H2	0	2.5711
S_h2s	278.00	3.7100

Table S3. LJ potential parameters for the atoms of the MOF and H₂S studied in this work.

Table S4. Atomic Partial Charges for the MIL-53(Al)-TDC and H₂S.

Atom Type	Charge	Atom Type	Charge
		~ 1 •	
Cl	0.58	S_h2s	-0.252
C2	-0.11	H_h2s	0.126
C3	-0.16		
01	-0.54		
02	-1.03		
H1	0.145		
H2	0.42		
S	0.08		
Al	1.78		

Details of Monte Carlo Simulations

Monte Carlo simulations in the NVT ensemble were carried out at 303 K to predict the adsorption behavior and identify the preferential adsorption sites of H_2S at low, intermediate and high loading. A simulation box was made of 12 unit cells (2×4×2) for the computational simulations, by fixing all atoms of the framework in their initial positions. These studies involved the analysis of the radial distribution functions plotted between different MOF/guest atoms pairs calculated for hundreds of MC configurations. The adsorption enthalpies at low coverage were calculated using the revised Widom test particle insertion.¹³



Simulated distribution of the H₂S molecules within the pores

Fig. S18. Snapshots extracted from MC simulations for different loads of H₂S: (a) 0.5 mmol g⁻¹, (b) 2.3 mmol g⁻¹, (c) 4.6 mmol g⁻¹, (d) 9.2 mmol g⁻¹ and (e) 18.5 mmol g⁻¹. The distances are reported in Å. (Al, pink; O, red; S, yellow; C, grey; H, white). (Interaction (Dashes lines): S_{H2S} -H_{µ2-OH}(blue), H_{H2S}-C_{org}(red), S_{H2S} -H_{H2S}(green)).

Radial distribution functions



Fig. S19. Radial distribution functions for the pair (a) C_{org} -H_{H2S}, (b) S_{H2S}-H_{H2S} and (c) H_{µ2-OH}-S_{H2S} at different loads of H₂S. (0.5 mmol g⁻¹, black; 2.3 mmol g⁻¹, red; 4.6 mmol g⁻¹, green; 9.2 mmol g⁻¹, blue and 18.5 mmol g⁻¹, pink).

8. PXRD under an atmosphere of H₂S



Fig. S20. in situ PXRD experiments under an atmosphere of H₂S recorded over time.

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