Supporting Information for:

SO$_2$ capture enhancement due to confined methanol within MOF Material MIL-53(Al)-TDC.

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S1. Experimental Details

Materials synthesis

Reagents were purchased from commercial suppliers and used without further purification.

MIL-53(Al)-TDC, was synthesised according to the protocol reported in the literature.[1] A solution of H_2BDC (62 mg, 0.036 mmol) and $AlCl_3$ (64 mg, 0.048 mmol) in DMF (1.8 mL) and H_2O (2.5 mL) was heated up at 100 °C for 5 hours inside of 20 mL pressure tube. Then, at the end of the reaction time, the reaction mixture was cooled down to room temperature, the reaction crude was filtered under vacuum and washed with DMF to obtained as-MIL-53(Al)-TDC. The activation process involved heating the sample up at 150 °C for 1 hour to obtain as-MIL- 53(Al)-TDC. Then, acetone-exchange was applied to remove DMF molecules, and the sample was heated up at 200 °C under vacuum for 4 hours. This product was characterized by PXRD and N_2 adsorption.

PXRD

Powder X-Ray Diffraction Patterns (PXRD) were recorded on a Rigaku Diffractometer, Ultima IV with a Cu-Kα_1 radiation (λ = 1.5406 Å) using a nickel filter. Patterns were recorded in the 25–50° 2θ range with a step scan of 0.02° and a scan rate of 0.08° min^{-1}.

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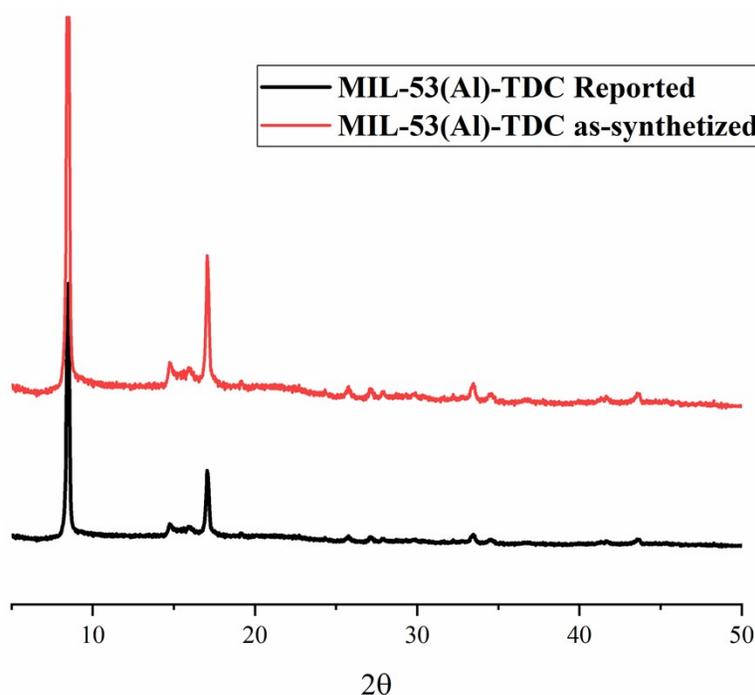
Figure S1. Experimental (red line) and reported[1] (black line) powder X-ray diffraction (PXRD) patterns for as-MIL-53(Al)-TDC.

Nitrogen adsorption isotherm

N_2 isotherms (up to $P/P_0 = 1$ and 77 K) were recorded on a Quantachrome Autosorb MP-1 equipment under high vacuum in a clean system with a diaphragm pumping system.
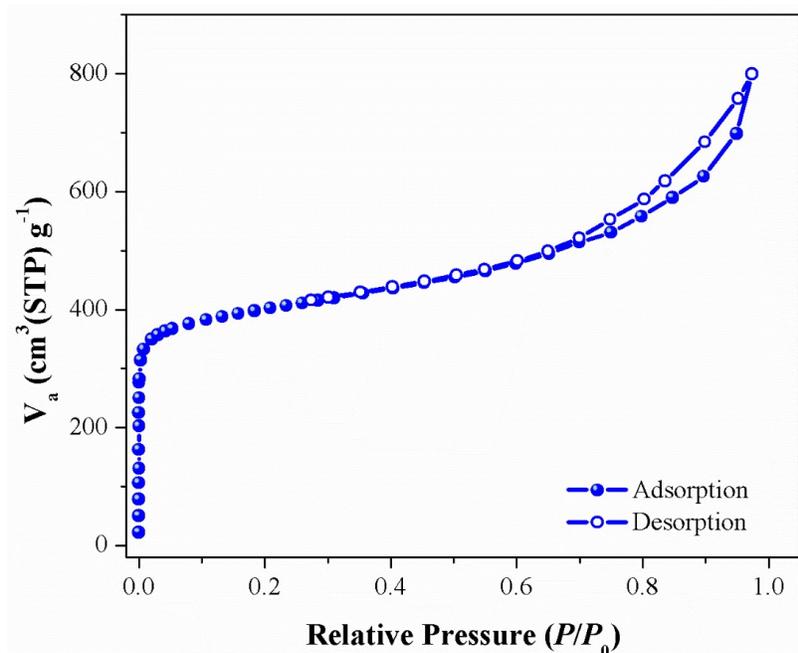
Figure S2. N_2 adsorption isotherm at 77 K of the as-synthesized MIL-53(Al)-TDC.

MeOH@MIL-53(Al)-TDC sample preparation:

Samples of acetone-exchanged MIL-53(Al)-TDC were placed in a quartz sample holder inside a DVS Advantage 1 microbalance module, and activated at 453 K for 2 h. After that time, the samples were cooled down to room temperature (under a flow of N2). Once activated, each sample was soaked in methanol vapour with the help of the previously mentioned device, selecting different values of partial pressure (2.26, 2.46, 2.68 and 2.76 % *P/P0*) in order to achieve the desired weight percentage for this investigation (2.05 wt %). The change in mass of the samples was monitored until the total mass reached a value consistent with the desired mass percentage of confined alcohol.

Results and Discussion

S2. SO₂ adsorption data
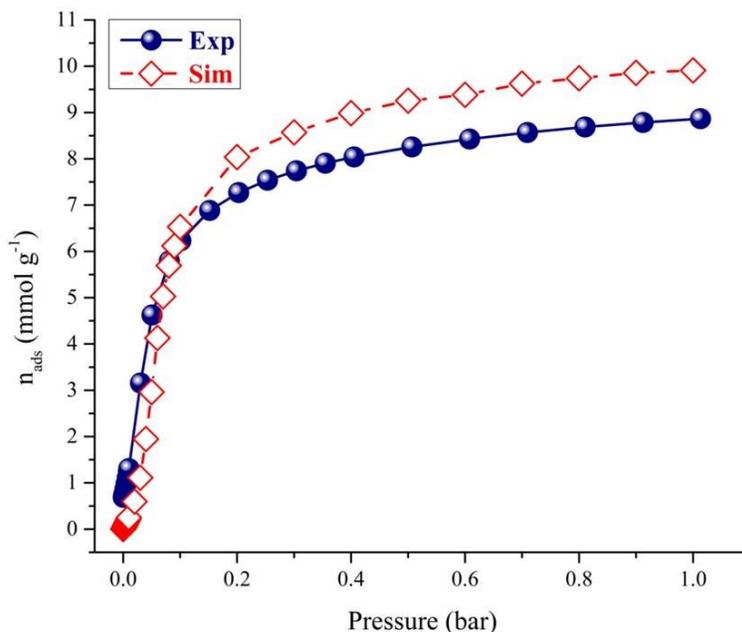
Figure S3. Comparison between the experimental (filled blue circles) and the GCMC simulated (open red rhombus) SO_2 adsorption isotherms at 298 K.

S3. Computational studies

Microscopic models for MIL-53(Al)-TDC, SO₂ and MeOH interatomic potential.

Initial atomic coordinates for MIL-53(Al)-TDC were taken from a previously reported study[1]. The Lennard-Jones (LJ) parameters for the organic and inorganic parts for MIL-53(Al)-TDC were taken from the DREIDING[2] force field and the UFF[3] force field 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[4] method as implemented in Dmol[3] and the Perdew–Burke–Ernzerhof (PBE)[5] functional and the DNP[6] basis set. The SO_2 molecule was represented by the atomistic model reported by Ketko *et. al.*[7] This corresponds to a rigid model where both three charged LJ sites are centered in the atomic positions, with a S-O bond of 1.432 Å and a O-S-O bond angle of 119.3°. On the other hand, the MeOH was represented by the CHARMM model[8]. This model has six charged LJ sites centered in the atomic positions, with a C-H bond of 1.111 Å and a H-C-H bond angle of 108.4 °, additionally the model has the bond distances for C-O bond of 1.42 Å and O-H bond of 0.96 Å and the C-O-H angle of 106.0°. The MOFs-SO_2/MeOH interactions were

described using a 12-6 LJ potential and a coulombic contribution. Using a general approach adopted in previous studies,[9] the H atom from the μ-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.[10]
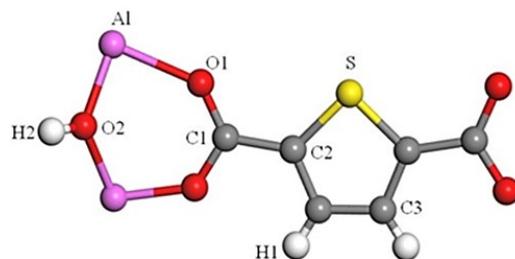
Fig. S4. Labels of the atoms for the organic and inorganic parts of MIL-53(Al)-TDC.

Table S1. LJ potential parameters and charges for the atoms of the MIL-53(Al)-TDC.

Atom Type	ε (K)	σ (Å)	Charge
Al	0	4.0081	1.78
S	137.88	3.5948	0.08
C1	47.856	3.4729	0.58
C2	47.856	3.4729	-0.11
C3	46.856	3.4729	-0.16
O1	48.158	3.0331	-0.54
O2	30.193	3.1181	-1.03
H1	7.6489	2.8464	0.145
H2	0	2.5711	0.42

Table S2. LJ potential parameters and charges for the atoms of the SO_2 and MeOH.

Atom Type	ε (K)	σ (Å)	Charge
S_so2	73.800	3.3900	0.590
O_so2	79.000	3.0500	-0.295
CH3	39.251	3.6527	-0.390

HC3	12.077	2.3875	0.090
OH	96.668	3.1449	-0.650
HO	23.148	0.4000	0.419

The simulation box consisted of 16 unit cells (2×4×2) for MIL-53(Al)-TDC, by fixing all atoms of the framework in their initial positions. All Monte Carlo (MC) simulations were performed using the simulation code CADSS (Complex Adsorption and Diffusion Simulation Suite),[11] using 2.0×10^7 MC steps for each pressure point. MC simulations in the μVT ensemble were carried out at 298 K to predict the adsorption behavior of SO_2 in the range of 0.0001 to 1 bar. The fugacity used for each of the simulations was calculated using the Peng-Robinson equation of state. Complementary MC simulations were carried out in the NVT ensemble at 298 K to explore the preferential adsorption sites of SO_2 at low, intermediate and high loading. 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 also calculated using the revised Widom test particle insertion.[12]

Radial Distribution Functions
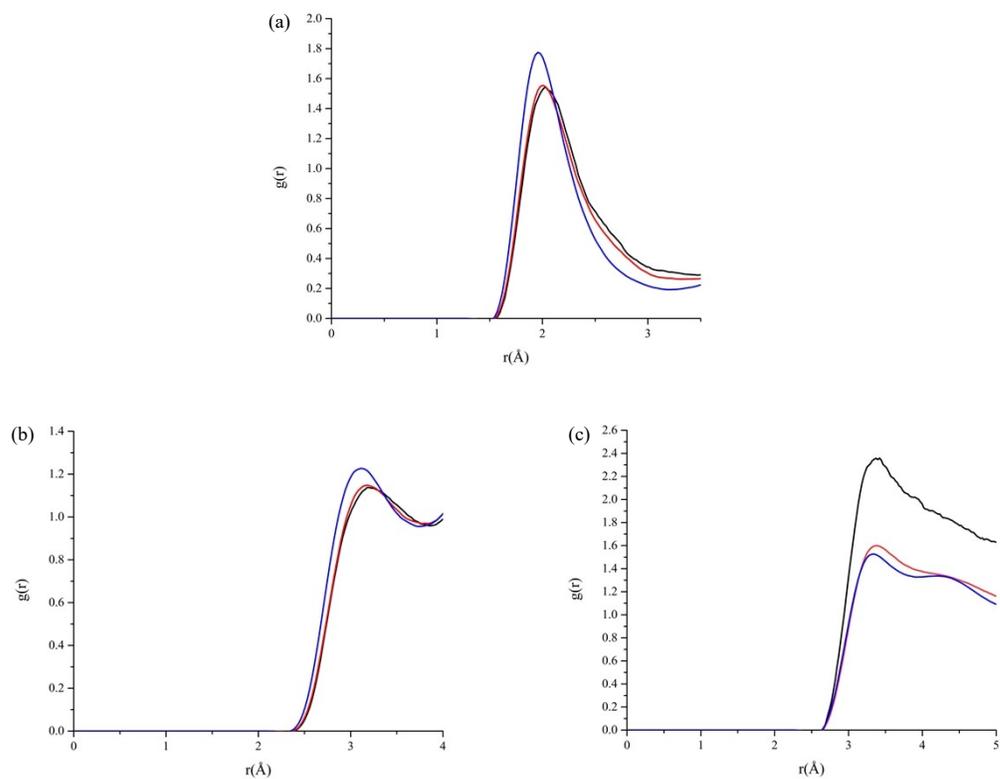
Fig. S5. Radial distribution functions obtained from the MC simulations in MIL-53(Al)-TDC for the pair (a) $H_{\mu\text{-}OH}$-O_{SO2}, (b) H_{org}-O_{SO2} and (c) S_{So2}-O_{SO2} at different loads of SO_2. (1.1 mmol g^{-1}, black; 5.0 mmol g^{-1}, red; 9.1 mmol g^{-1}, blue).

S6. References

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