Supporting Information

Probing the adsorption performance of the hybrid porous MIL-68(Al): A synergic combination of experimental and modelling tools

Qingyuan Yang,[a,b] Sébastien Vaesen,[c] Muthusamy Vishnuvarthan,[d] Florence Ragon,[e] Christian Serre,[e] Alexandre Vimont,[d] Marco Daturi,[d] Guy De Weireld,*[c] Guillaume Maurin*[b]

[a] State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

[b] Institut Charles Gerhardt Montpellier, UMR CNRS 5253, UM2, ENSCM, Place E. Bataillon, 34095 Montpellier cedex 05, France.

E-mail: guillaume.maurin@univ-montp2.fr

[c] Faculté Polytechnique de Mons, Université de Mons, Place du Parc 20, 7000 Mons, Belgium

Email: guy.deweireld@umons.ac.be

[d] Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, 14050 Caen cedex, France

[e] Institut Lavoisier, UMR CNRS 8180-Université de Versailles St Quentin en Yvelines, 45 avenue des Etats-Unis, 78035 Versailles, France

1. Characterization of the synthesized MIL-68(Al) sample

1.1 X-Ray diffraction (XRD)

Phase identification and crystallinity check up of the phase were performed using a Siemens diffractometer D5000, it is a theta/theta2 diffraction instrument operating in reflection geometry using Cu Kalpha1 radiation (λ= 1.54056Å). Fig. *S*1 shows the corresponding XRD powder pattern of the activated MIL-68(Al) product.

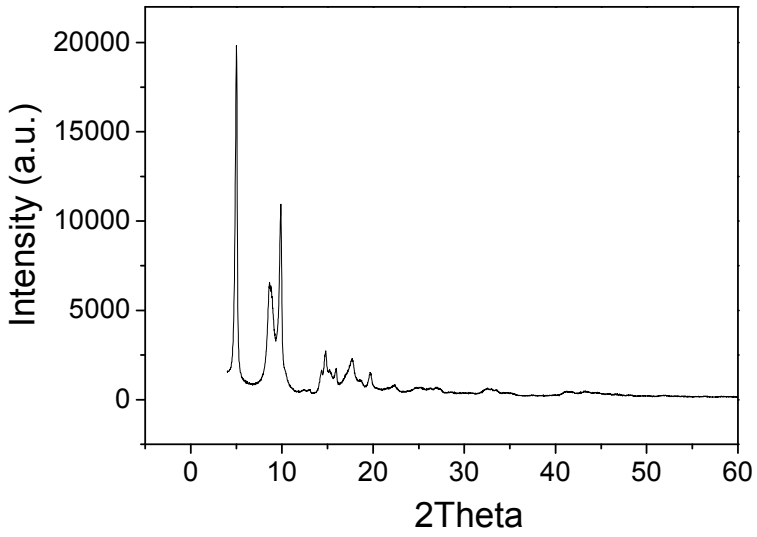


Fig. S1 *Experimental XRD powder pattern of the activated MIL-68(Al) sample.*

1.2 Infra-Red (IR) Spectroscopy

Fig. *S*2 shows the IR spectra, performed using a Nicollet spectrometer**,** of the activated product. The Infrared spectra clearly shows the presence of the vibrational bands characteristic of the carboxylates groups ($\nu_{C=O}$) at around 1430 and 1550cm^{-1} confirming the presence of the dicarboxylate within MIL-68(Al). No bands corresponding to the DMF (~1650cm^{-1}) are observed but a band around 1700cm^{-1} indicates there is still the presence of free acid in the material.

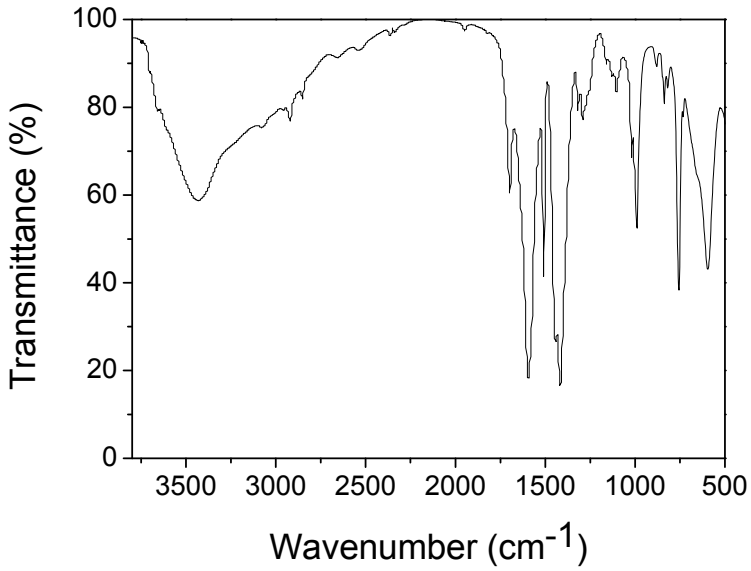


Fig. S2 *IR spectra of the activated MIL-68(Al) sample.*

1.3 Thermo gravimetric analysis (TGA)

Two weight-loss steps were observed on the TGA curve, performed using a Perkin Elmer, STA 6000 instrument: first the departure of the guest molecules (H_2O, MeOH and DMF) in the range 298 – 623 K (8.5%); the second one around 773 K is due to the decomposition of the framework to produce Al_2O_3 and associated with the departure of the organic linker (experimental: 67.8%; calculated: 69.5%).

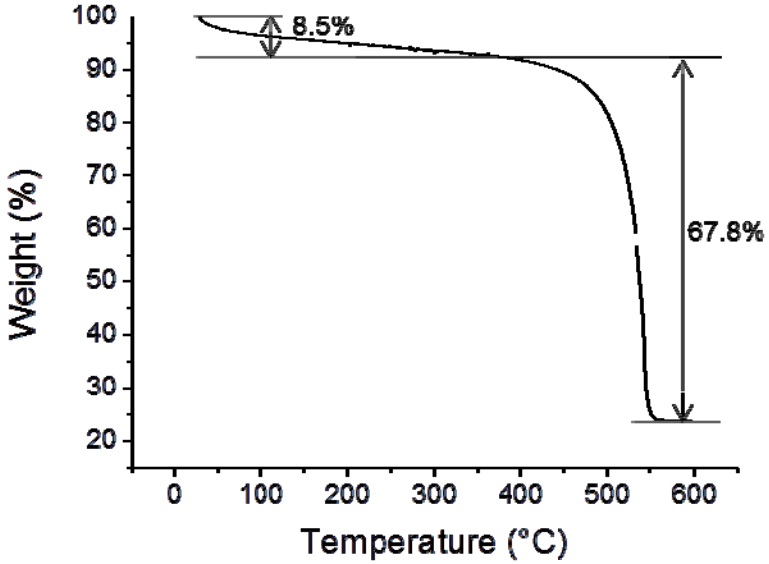


Fig. S3 *TGA curve of activated MIL-68(Al) product under O_2 (heating rate of 2 K per minute) (5mg of solid).*

1.4 Nitrogen porosimetry

Typical nitrogen sorption isotherm at 77K has been performed on the material after a treatment under primary vacuum at 423 K overnight (BEL Japan, BELSORP Prep). A BET specific surface area of 1430(20) $m^2.g^{-1}$ is obtained.

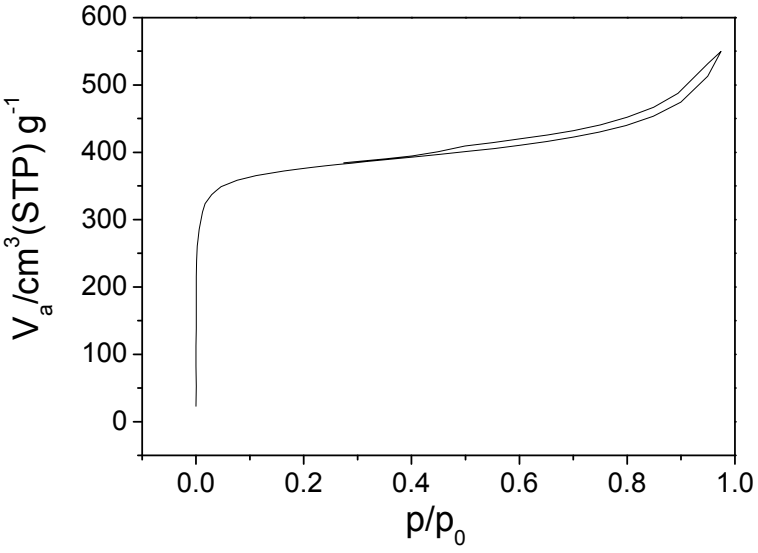


Fig. S4 *Nitrogen adsorption isotherm of the MIL-68(Al) at T = 77 K (p_0 = 1 atmosphere).*

2. Atomic partial charges obtained by DFT calculations

2.1 Model Cluster and atomic partial charges of MIL-68(Al)

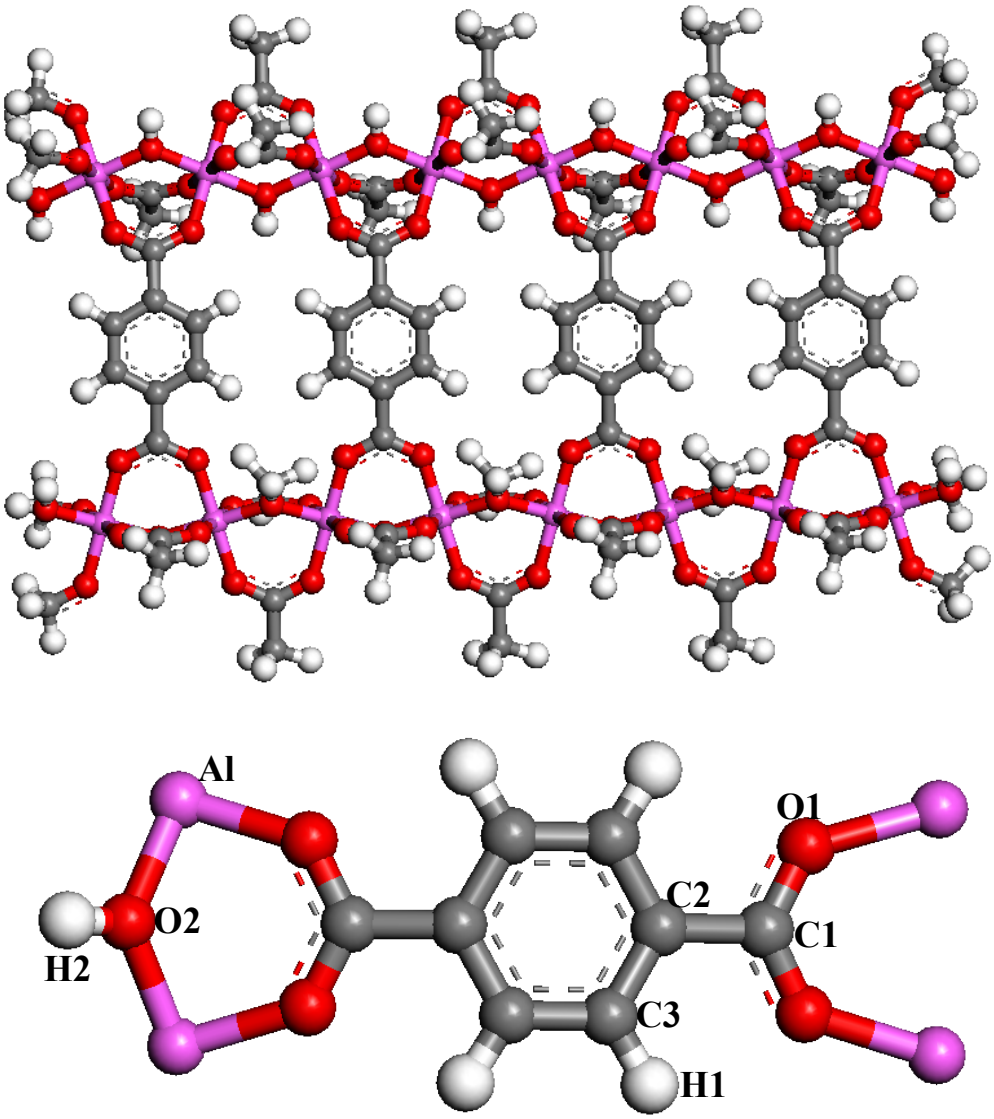


Fig. S5. *Cluster used for calculating the partial charges on MIL-68(Al) atoms. To minimize the boundary effects, the terminal Al atoms were saturated with two methoxyl and one hydroxyl groups, while other terminations were saturated by methyl groups.*

***Table S1*. Atomic partial charges for the MIL-68(Al) structure derived on DFT/PBE Level.**

Atomic types	Al	O1	O2	C1	C2	C3	H1	H2
Charge (*e*)	1.817	-0.584	-1.072	0.572	0.036	-0.144	0.126	0.447

2.2 Model cluster and atomic partial charges of MIL-68(Al)-NH_2

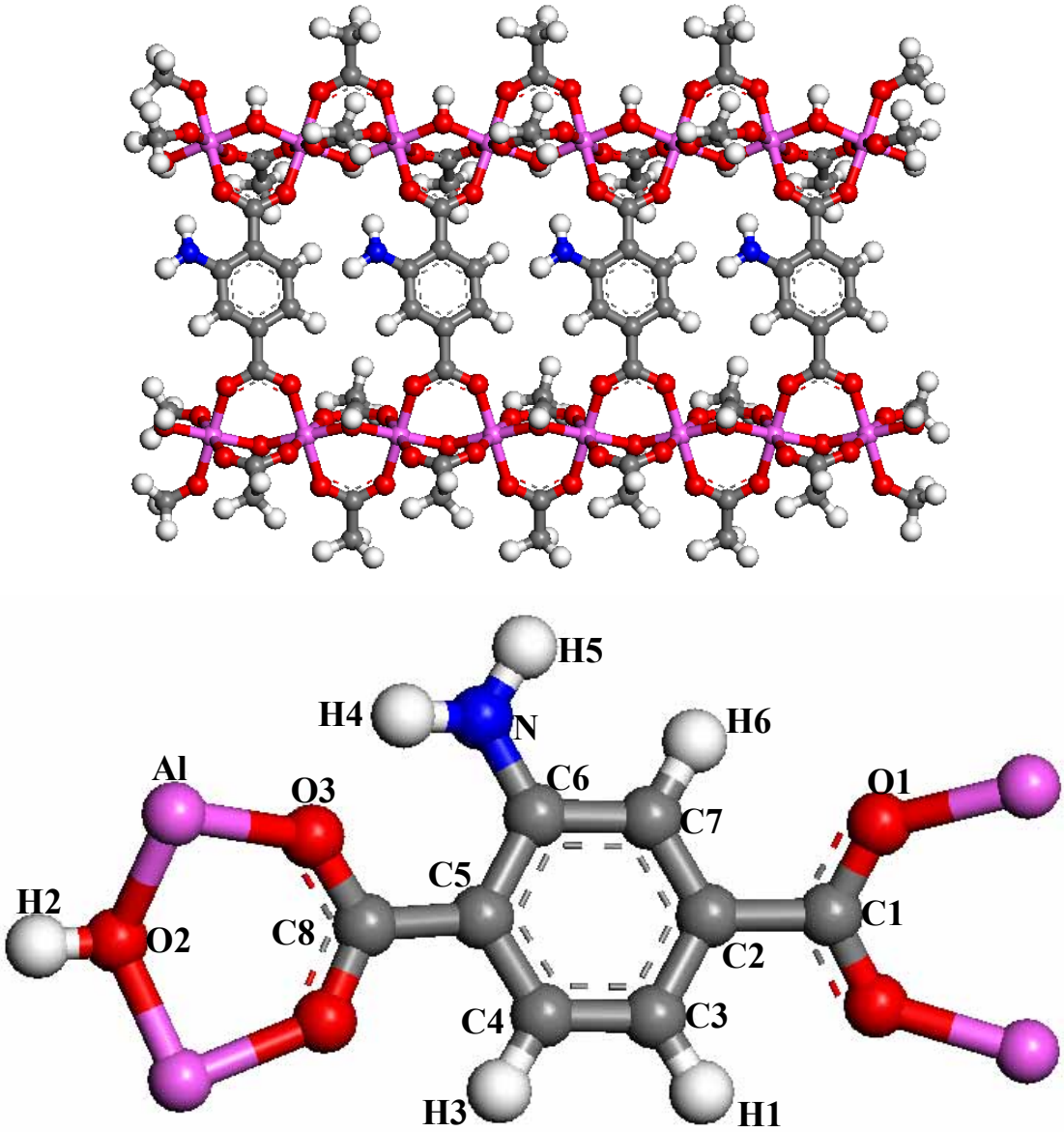


Fig. S6. *Cluster used for calculating the partial charges on MIL-68(Al)-NH_2 atoms. To minimize the boundary effects, the terminal Al atoms were saturated with two methoxyl and one hydroxyl groups, while other terminations were saturated by methyl groups.*

***Table S2*. Atomic partial charges for the MIL-68(Al)-NH_2 structure derived on DFT/PBE Level.**

Atomic types	**Al**	**O1**	**O2**	**O3**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Charge (e)	1.845	-0.639	-1.057	-0.599	0.656	0.089	-0.309	0.023	-0.370	0.533
Atomic types	**C7**	**C8**	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**N**	
Charge (e)	-0.395	0.713	0.152	0.442	0.080	0.415	0.376	0.178	-0.895	

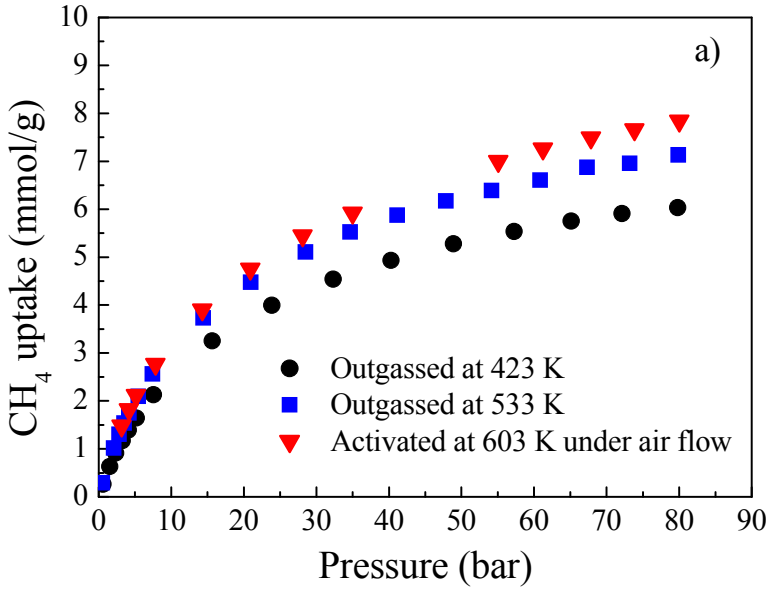
2.3 Mulliken partial charges for the MIL-68(Al) obtained by periodic DFT calculation

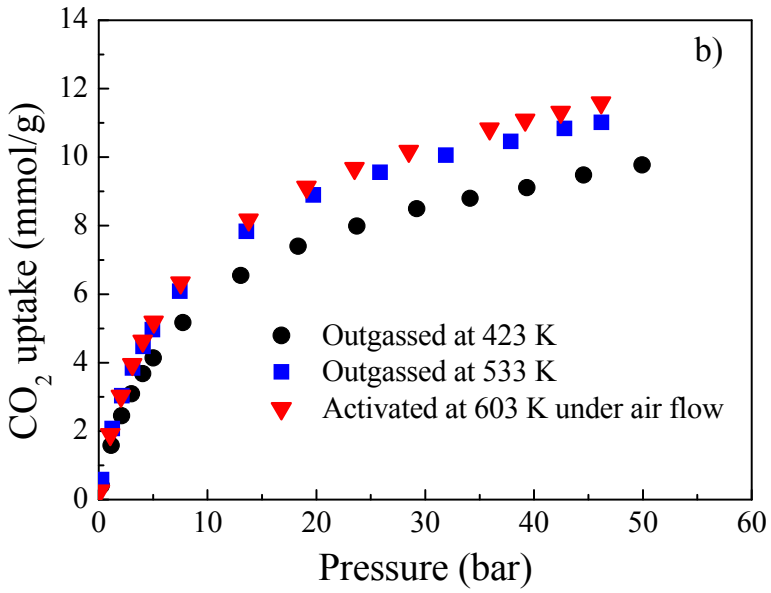
Table S3. Mulliken partial charges for the MIL-68(Al) structure derived on DFT/PW91 Level.

Atomic types	Al	O1	O2	C1	C2	C3	H1	H2
Charge (*e*)	1.403	-0.552	-0.718	0.567	-0.066	-0.088	0.143	0.301

3. Adsorption isotherms

3.1 Experimental adsorption isotherms at 303 K





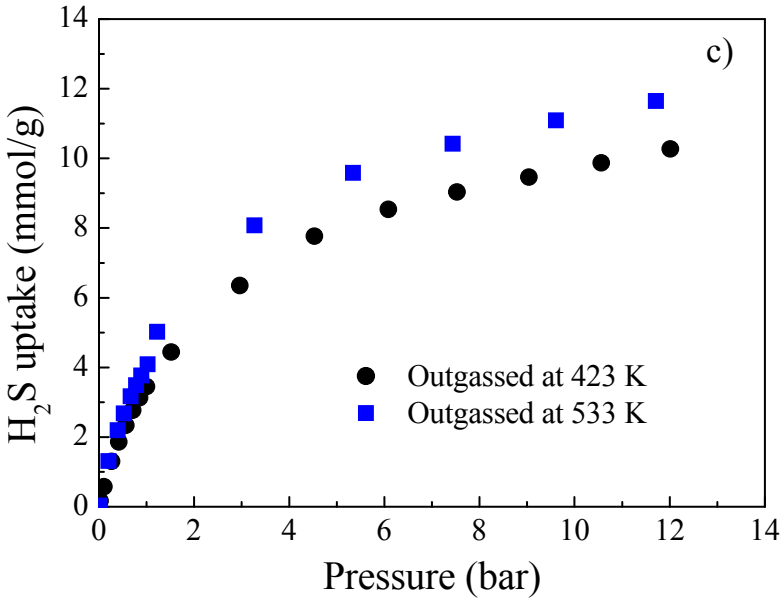


Fig. S7. *Influence of the activation temperature on the absolute adsorption isotherms in the MIL-68(Al) at 303 K: (a) CH_4, (b) CO_2 and (c) H_2S.*

3.2 Simulated adsorption isotherms of N_2 in the MIL-68(Al) at 303 K

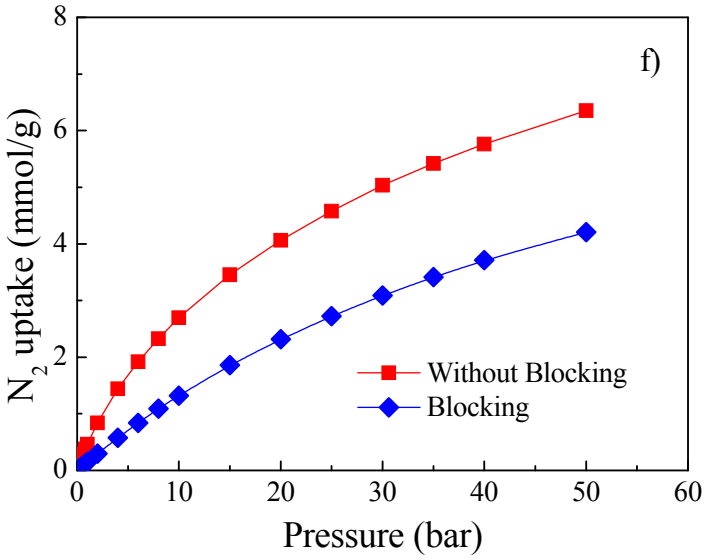
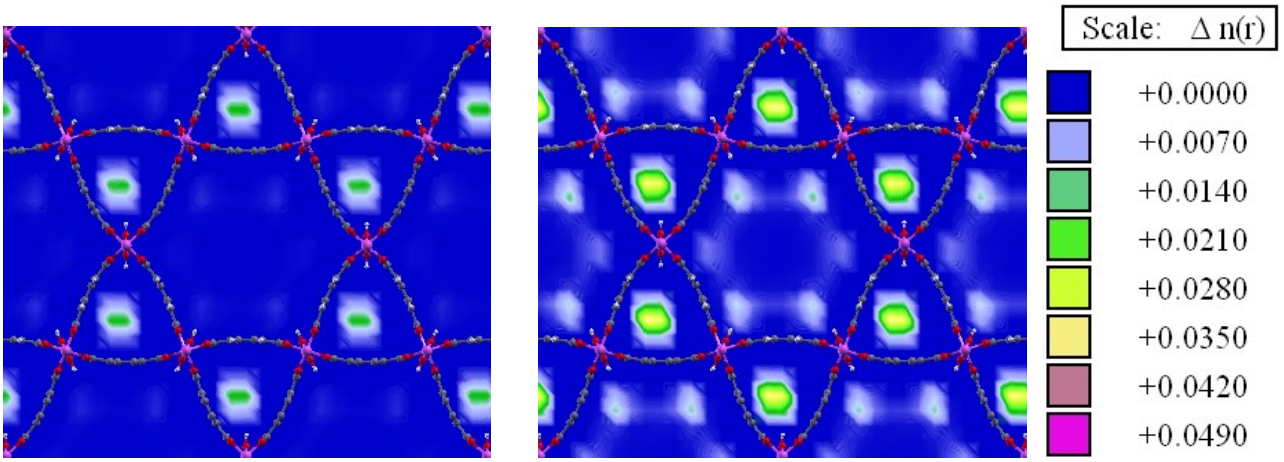


Fig. S8 *Effect of blocking the triangular pores on the simulated absolute adsorption isotherms of N_2 in the MIL-68(Al) solid at 303 K. These results were obtained using ESP charges combined with DREIDING forcefield.*

4. Microscopic adsorption mechanism of CO_2 in the MIL-68(Al) at 303 K



a) P = 0.1 bar **b) P = 1.0 bar**

c) P = 10.0 bar **d) P = 50.0 bar**

Fig. S9. *Contour plots of the probability density distributions of the COM of CO_2 in MIL-68(Al) at different pressures, viewed along the direction of the channels.*

5. Radial Distribution Functions (RDFs) and snapshots in the MIL-68(Al) with the triangular channels blocked

5.1 RDFs and snapshot for CO_2 molecules

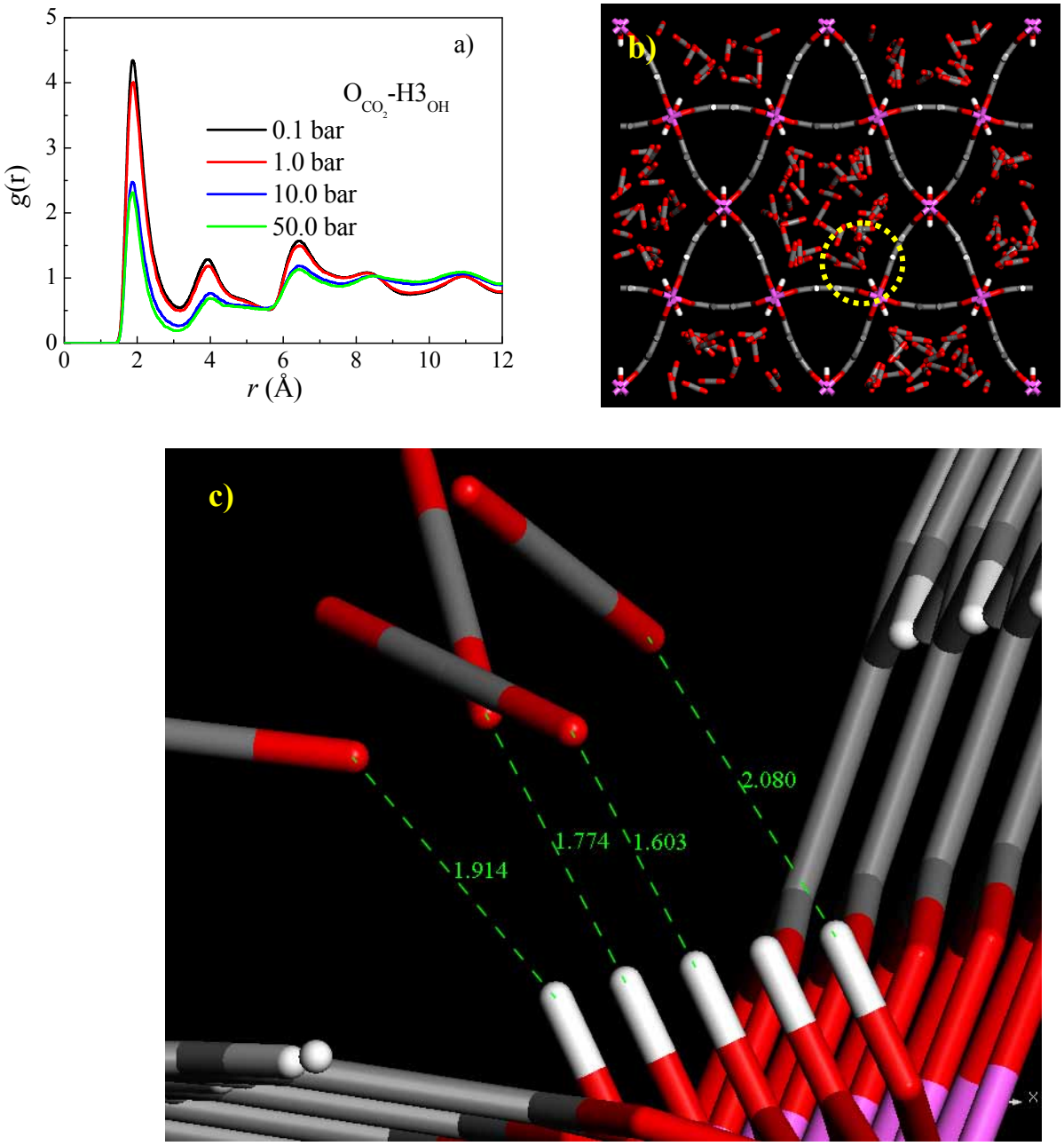


Fig. S10. *(a) RDFs of CO_2 molecules around the H atoms of the –OH groups (denoted as $H3_{OH}$) in the hexagonal channels in the MIL-68(Al) at different pressures, (b) One typical snapshot for the CO_2 molecules adsorbed at 10.0 bar, where a close-up view of the part marked with the yellow circle is shown in (c). These results were obtained from the simulations with blocking the triangular channels.*

5.2 RDFs and snapshot for H_2S molecules

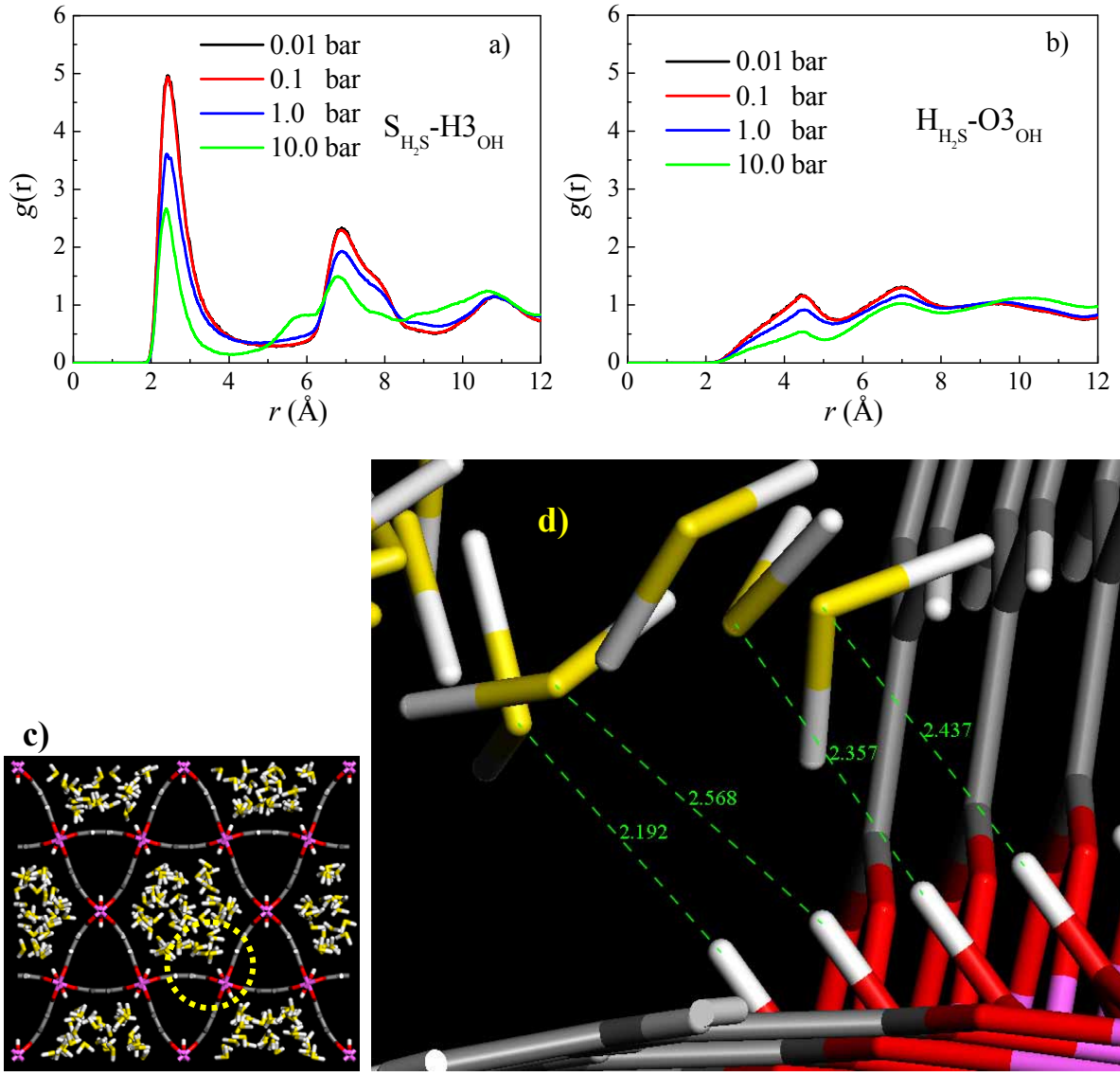


Fig. S11. *RDFs of the (a) S atoms in the H_2S molecules around the H atoms (denoted as $H3_{OH}$) and (b) H atoms in the H_2S molecules around the O atoms (denoted as $O3_{OH}$) of the –OH groups in the hexagonal channels in the MIL-68(Al) at different pressures; (c) One typical snapshot for the H_2S molecules adsorbed at 10.0 bar, where a close-up view of the part marked with the yellow circle is shown in (d). These results were obtained from the simulations by blocking the triangular channels.*

6. RDFs calculated in the MIL-68(Al) without blocking the triangular channels

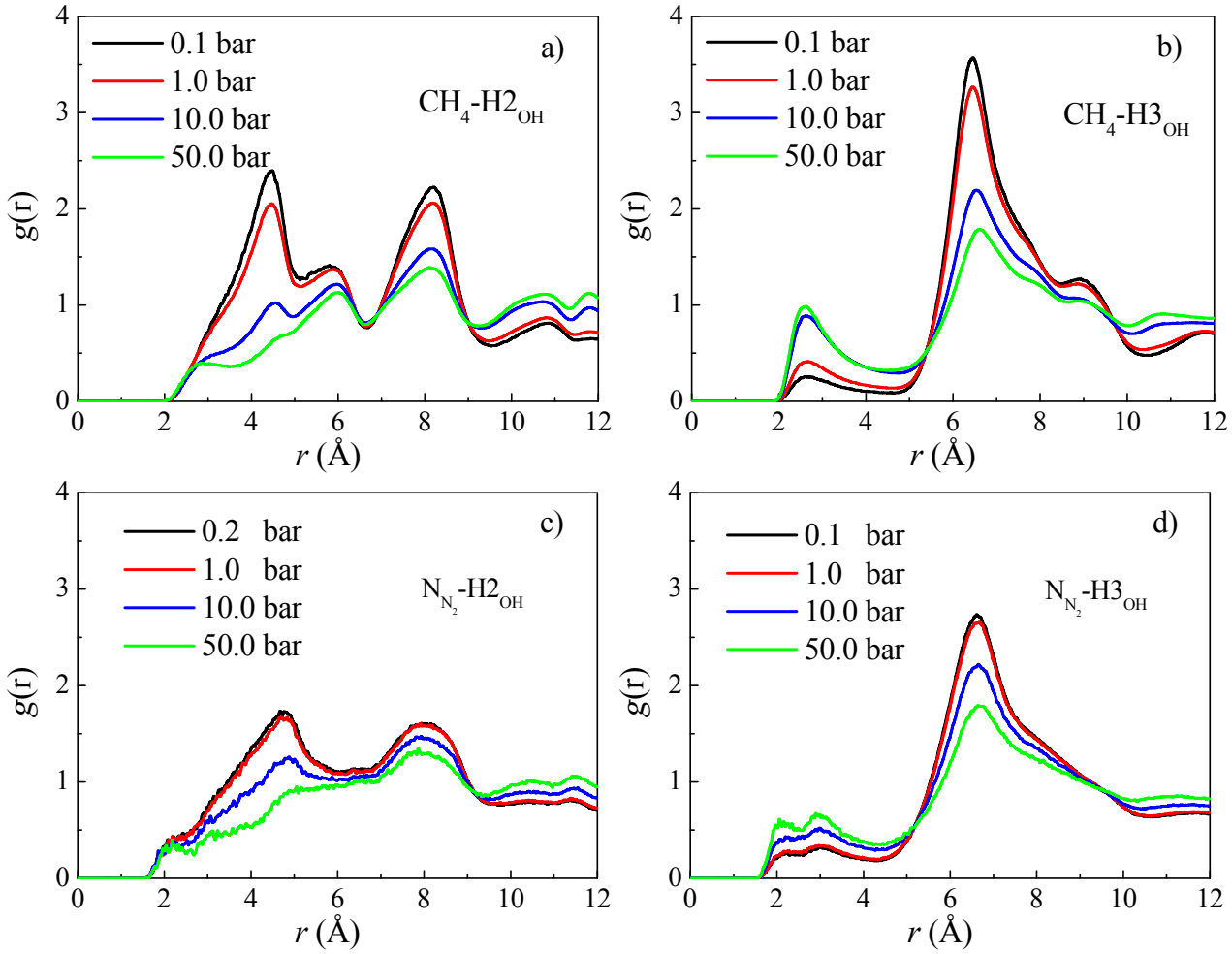


Fig. S12. *RDFs of the CH_4 (a, b) and N_2 (c, d) molecules around the H atoms of the –OH groups in the triangular (denoted as $H2_{OH}$) and hexagonal (denoted as $H3_{OH}$) channels in the MIL-68(Al) at different pressures. These results were obtained from the simulations without blocking the triangular channels.*