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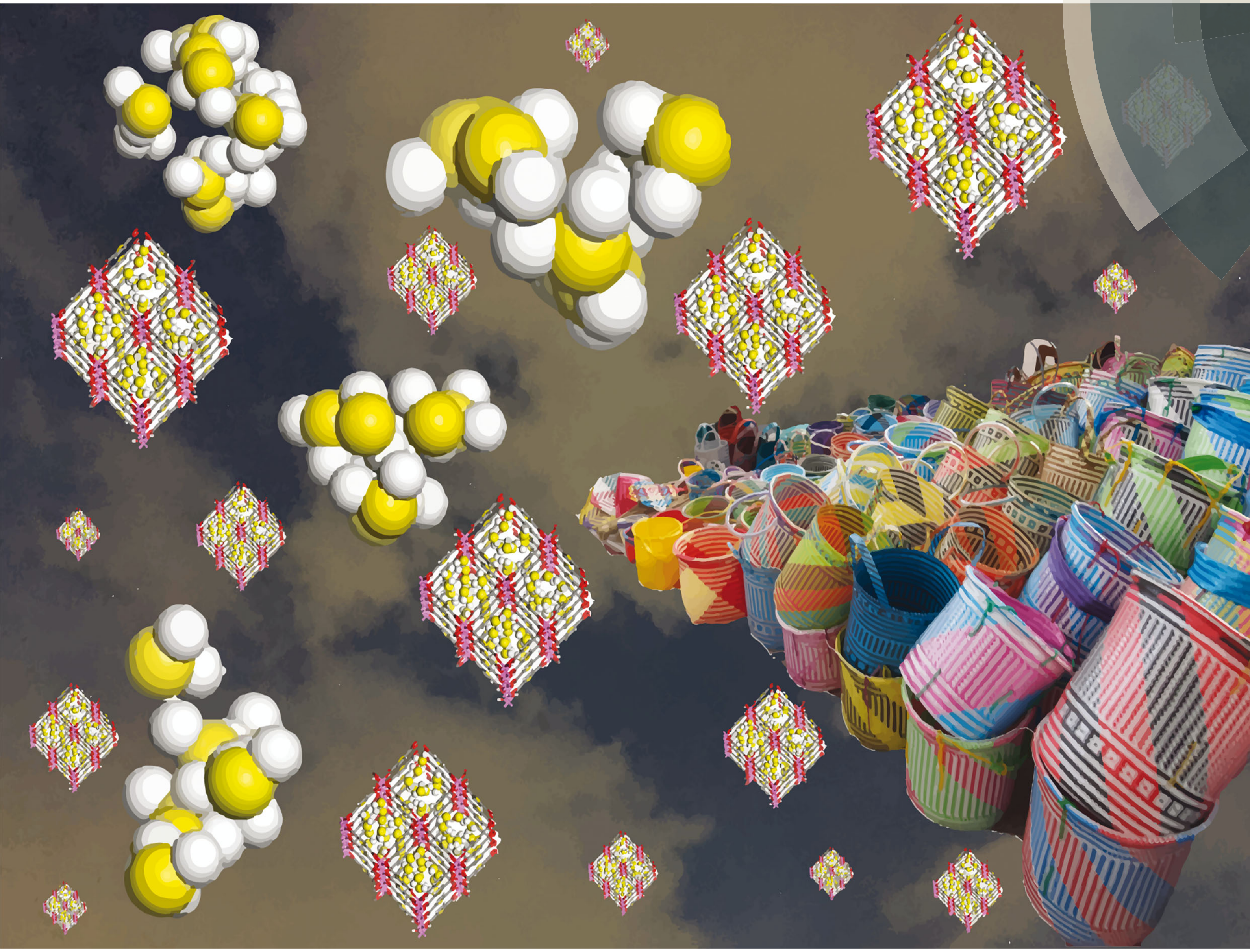

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The MOF-type MIL-53(Al)-TDC was demonstrated to be an optimal adsorbent for H_2S capture combining an unprecedented uptake at room temperature, excellent cyclability and low-temperature regeneration.

Hydrogen sulphide (H_2S) is a harmful chemical present in natural gas and biogas, and emitted by different chemical industries, *e.g.*, the oil desulfurization process at oil refineries.[1] H_2S is considered as a major air pollutant due to its negative environmental impact, mainly associated with acid rain,[2] and high toxicity to humans leading to severe nervous system illnesses.[3] Current techniques to capture and separate H_2S include reactive and non-reactive absorption (*e.g.*, alkanolamines and ionic liquids), adsorption (*i.e.*, zeolites, metal oxides and activated carbons), membrane separation (polymeric and ceramic) and cryogenic distillation.[1b] In the field of adsorption, the development of new and emerging sorbents capable of capturing high amounts of H_2S (*via* physisorption processes) is increasingly investigated.[4] Typically, a hybrid TiO_2/zeolite composite demonstrated a total H_2S capacity of 0.13 mmol g^{-1},[4b] with regeneration achieved by basic washing and calcination, which is an inefficient energy process.[4b] Alternatively, alkaline activated carbon materials[4c] demonstrated a higher H_2S uptake of 6.18 mmol g^{-1}, however, associated with a lesser regeneration due to the chemisorption phenomenon. Different hybrid porous materials, namely Metal–Organic Frameworks (MOF), have been envisaged for the capture of H_2S; however, some of them have the main disadvantage of showing poor chemical stability.[5] For example, De Weireld *et al.*[5b] investigated the H_2S adsorption properties of an extensive series of MIL-*n* porous materials and they reported the structural collapse of MIL-53(Fe) due to the formation of iron sulfide. Zou[6] and Eddaoudi[7] also demonstrated the decomposition of diverse MOF materials (Zn-MOF-74, Cu-BTC, MOF-5, MIL-100(Fe) gel, In-soc-MOF and Fe-soc-MOF) upon H_2S adsorption. Conversely, Bordiga *et al.*[8] reached a 4.98 mmol H_2S g^{-1} capture in MOF-74(Ni) observing a high stability of the material by powder X-ray diffraction (PXRD). However, chemically stable MOF materials that exhibit open metal sites (*e.g.*, MOF-74), or other functional groups, often show difficulty to desorb H_2S due to very high host–guest binding within the pores either *via* strong physisorption or even by chemisorption. Thus, desorption of H_2S is unwittingly accompanied by an undesirable large energy penalty.[9] Moreover, an ideal H_2S adsorbent needs to demonstrate high H_2S cyclability under industrially practical pressure-swing desorption conditions.[10] So far, the MOF Ni-CPO reported by Morris *et al.*[11] shows the highest H_2S uptake performance, *i.e.* 12.0 mmol g^{-1} (at 30 °C and 1 bar), without any degradation of its crystalline structure. Although they demonstrated a small loss of gas capacity over a six-month period, a comprehensive regeneration study was not presented.[11]

Recently, Stock *et al.*[12] reported the synthesis of a water-stable microporous MOF material entitled MIL-53(Al)-TDC [Al(OH)TDC]. This Al-based MOF is constructed using 2,5-thiophenedicarboxylate (TDC) ligands and Al(III)-oxygen octahedra [AlO_4*trans*-(μ-OH)$_2$], and crystallises in the *Pmna* space group. Each Al(III) centre is coordinated by six oxygen atoms from four different TDC ligands and two hydroxyl (μ-OH) groups (Fig. S1, ESI†). The overall framework structure of MIL-53(Al)-TDC shows square shape channels with a diameter of approximately 9.2 × 8.9 Å

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† Electronic supplementary information (ESI) available: Crystal structure of MIL-53(Al)-TDC, experimental, PXRD and SEM experiments after H_2S, H_2S breakthrough experiments on known MOF materials, H_2S desorption by Hi-Res TGA and molecular simulations. See DOI: 10.1039/c8cc09379b

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(Fig. S1, ESI†). This material has been previously evaluated, by our group, for CO_2 capture[13] and very recently Janiak and co-workers[14] demonstrated its promising properties in regard to heat transformation applications. Herein, MIL-53(Al)-TDC is demonstrated to exhibit the highest H_2S capture ever reported for any adsorbent to the best of our knowledge along with the retention of its crystalline structure after multiple H_2S adsorption/desorption cycles and an excellent regeneration at relatively low temperature. Advanced experimental and computational tools have been further coupled to gain insights into the molecular mechanisms responsible for this spectacularly high and reversible adsorption behaviour.

The adsorption of H_2S by MIL-53(Al)-TDC (activated at 200 °C for 4 hours under a flow of dry N_2 gas) was evaluated by a series of breakthrough experiments and corroborated by gravimetric measurements both at 30 °C and 1 bar (see Experimental ESI,† Fig. S4–S6). The adsorption capacities obtained are reported in Table S1 and Fig. S4 (ESI†). In the breakthrough experiments, the H_2S concentration studied (5 vol% H_2S, 95 vol% N_2) led to a gas uptake equal to 18.13 mmol H_2S g^{-1}, *i.e.* 618 mg H_2S g^{-1} (see Fig. 1, first cycle), which corresponds to 585 cm^3 H_2S g^{-1}. This outstanding H_2S adsorption capacity is by far the highest value reported at 30 °C and 1 bar for a MOF material, to the best of our knowledge, since this uptake is about 66% higher than the record reported by Morris *et al.*[11]

To validate our experimental H_2S breakthrough system, we assessed the H_2S adsorption performances of previously reported MOFs, *i.e.*, Mg-CUK-1: 1.4 mmol g^{-1}, MOF-74(Zn): 1.6 mmol g^{-1}, HKUST-1: 1.1 mmol g^{-1} and MIL-101(Cr): 0.4 mmol g^{-1}. Our in-house experimental setup exhibited very similar H_2S total captures to the existing data (see Fig. S12 and Table S2, ESI†), corroborating the reliability of our breakthrough measurements. Additionally, kinetic gravimetric H_2S uptake experiments were performed (see ESI†) with a total H_2S capture of 18.1 mmol g^{-1} (see Fig. S6, ESI†). This kinetic experiment was in good agreement with the total H_2S uptake obtained from the breakthrough experiments (18.5 mmol g^{-1}). Later, the H_2S saturated sample was re-activated (see Experimental ESI†) and another kinetic H_2S uptake experiment was carried out (as previously described), to reach a total H_2S capture of 18.6 mmol g^{-1}.

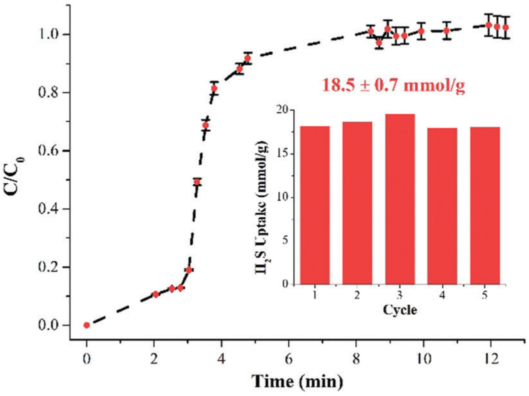

Fig. 1 Breakthrough curves of H_2S adsorption by MIL-53(Al)-TDC at 30 °C and 1 bar using a feed H_2S concentration of 5 vol%. The total H_2S/N_2 flow rate was 30 cm^3 min^{-1}. The inset shows the comparative adsorption capacities for each cycle.

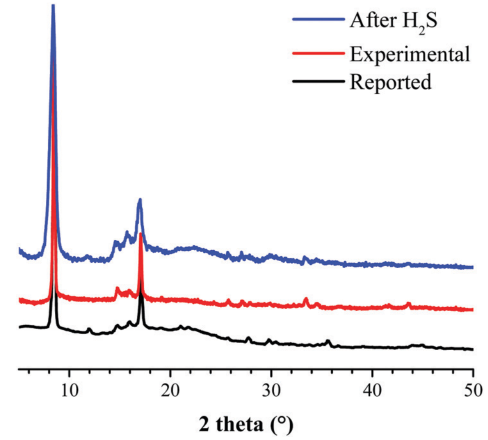

Fig. 2 PXRD patterns for the MIL-53(Al)-TDC sample before (red) and after the H_2S adsorption experiment (blue). Previously reported PXRD pattern (black).[12]

We further demonstrated that MIL-53(Al)-TDC retains its crystal structure upon H_2S exposure as evidenced by the PXRD analysis collected on the material after H_2S adsorption (see Fig. 2) and under an atmosphere of H_2S (see Fig. S20, ESI†). As a further step, we explored the H_2S regeneration-capacity of MIL-53(Al)-TDC, by cycling H_2S experiments at 5 vol% H_2S on the same MIL-53(Al)-TDC sample. Cycling adsorption–desorption results showed that the H_2S adsorption capacity remained constant during the five adsorption–desorption cycles (18.5 ± 0.7 mmol g^{-1}, Fig. 1), which suggests that H_2S was completely desorbed when the sample was re-activated (200 °C for 2 hours under a flow of dry N_2 gas, see Experimental: H_2S adsorption experiments ESI†) prior to any next adsorption cycle (see ESI†). The extremely high stability of the H_2S cycled MIL-53(Al)-TDC sample was further checked by PXRD, scanning electron microscopy (SEM) analyses and N_2 adsorption isotherms, confirming the retention of its crystal structure (Fig. S7–S11, ESI†).

Finally, a high definition TGA (High-Resolution technique, dynamic rate TGA) experiment (see Fig. S13, ESI†) was performed on this H_2S saturated sample showing a weight loss, from room temperature to 65 °C, corresponding to 18.6 H_2S mmol g^{-1}. This experiment confirmed not only the regeneration of the material, but more importantly the relatively low energy requirement (approximately 65 °C) to fully desorb H_2S.

In order to further investigate the interactions between H_2S and MIL-53(Al)-TDC, *in situ* DRIFT experiments were performed at 30 °C. Fig. 3 shows the IR spectra for MIL-53(Al)-TDC samples: before (activated sample, see Experimental) and after H_2S adsorption (under an atmosphere of H_2S). The activated sample showed a typical sharp absorption band, at 3698 cm^{-1}, assigned to the O–H stretching vibration mode of the μ-OH group bridged with two aluminium metal centres. Additional absorption bands, characteristic of the carboxylate groups in the 1600–1300 cm^{-1} region and at 3097 cm^{-1}, due to the C–H stretching vibration of the thiophene, were also found.[15] After the H_2S adsorption, an

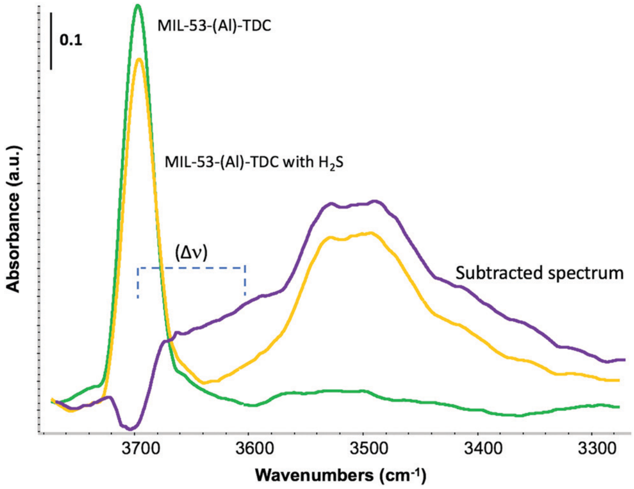

Fig. 3 DRIFT spectra at 30 °C of activated MIL-53(Al)-TDC (green); MIL-53(Al)-TDC after H_2S adsorption (yellow) and the subtracted spectrum (purple).

intense broad IR absorption band appeared at ~3491 cm^{-1}, suggesting the formation of hydrogen bonds between H_2S molecules themselves confined in the pores of MIL-53(Al)-TDC (see Fig. 3) similarly to what has been previously evidenced in the case of MIL-53(Cr) and MIL-47(V).[16] An additional weak band appeared at lower wavenumbers (2588 cm^{-1}, see Fig. S14, ESI†), which was assigned to the ν(S–H) vibration mode. A characteristic band from the stretching vibration of C–S bonds (thiophene ring) was identified at ~1113 cm^{-1} (Fig. S15, ESI†). The band at 3698 cm^{-1}, attributed to the μ-OH group, showed a small decrease in intensity. Precisely, the interactions between the μ-OH groups and H_2S molecules, lead to a shift of the maximum of the O–H stretching vibration band (approximately 3700 cm^{-1}) to a lower wavenumber (3618 cm^{-1}) as well as its broadening (see Fig. 3). By taking the DRIFT spectra difference, the subtracted spectrum showed a small negative band (see Fig. 3) (red shift of about 80 cm^{-1}) corresponding to only a relatively weak interaction between H_2S and the μ-OH groups. This observation might suggest that the adsorbed molecules can also interact with other functionalities of the MOF material, *e.g.*, the thiophene ring that could be responsible for the intense band observed at ~3491 cm^{-1}.

Finally, the corresponding H_2S adsorbed bands at ~3491 cm^{-1} and 1113 cm^{-1}, disappeared after only flowing dry N_2 gas (inside the DRIFT chamber) at room temperature. This indicated that the H_2S molecules were weakly adsorbed within the pores of MIL-53(Al)-TDC. Indeed, after flowing dry N_2 gas inside the DRIFT chamber, the so-obtained DRIFT spectrum was very similar to that of the pristine material, supporting a complete evacuation of H_2S (see Fig. S16, ESI†).

To gain further insight into the adsorption behavior of H_2S at the atomic level, Monte Carlo simulations were performed in the Canonical ensemble (*NVT*) for different loadings corresponding to the experimental findings.

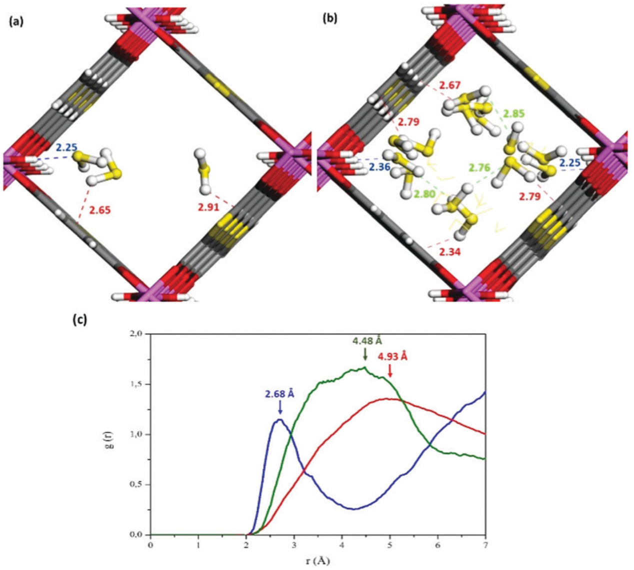

Fig. 4 Illustrative arrangements of H_2S in the pores of MIL-53-TDC generated from the MC simulations at (a) 0.5 mmol g^{-1} and (b) 18.5 mmol g^{-1}. (c) Radial distribution functions for the atom pairs $C_{org}–H_{H_2S}$, $S_{H_2S}–H_{H_2S}$ and $S_{H_2S}–H_{\mu\text{-OH}}$ (interactions: blue, $S_{H_2S}–H_{\mu\text{-OH}}$; red, $C_{org}–H_{H_2S}$ and green, $S_{H_2S}–H_{H_2S}$) calculated at saturation. The distances are reported in Å. (Al, pink; O, red; S, yellow; C, grey; H, white).

Our calculations evidenced that at low loading, H_2S interacts *via* its S-atom with the H-atom of the μ-OH group with a mean characteristic distance of 2.68 Å as defined by the plot of the radial distribution function (RDF) for the corresponding atom pair reported in Fig. 4c. This scenario corresponds to a relatively weak hydrogen bond interaction, which is reminiscent with what we already reported in other MOFs containing hydroxyl groups[5f,15,17] including MIL-125(Ti), MIL-53(Cr), MIL-68(Al) and CUK-1(Mg), and consistent with the IR findings. We have also revealed that H_2S also interacts with the thiophene linker associated with separating distances that are above 3 Å (see corresponding RDF Fig. 4c). Finally, the RDF for the $S_{H_2S}–H_{H_2S}$ pair evidences that the hydrogen bonds between the H_2S molecules are similar to that obtained in the previous MOFs.[5f,15,17] The guest molecules tend to arrange themselves along the channel in such a way to form dimers at high loading. An illustration of these interactions and the resulting arrangements of H_2S in the pores of MIL-53(Al)-TDC are provided in Fig. 4a and b at low and saturated loading, respectively. Furthermore, the H_2S adsorption enthalpy at low coverage was simulated to be −23.2 kJ mol^{-1} which corresponds to a moderate strength of host/guest interactions. This energetic behavior explains the IR findings and the easy regeneration of the material after H_2S adsorption.

In summary, MIL-53(Al)-TDC was established to be a highly robust MOF for the capture of acidic H_2S. MIL-53(Al)-TDC demonstrated the highest H_2S adsorption (18.1 mmol g^{-1}) ever reported for any adsorbent to the best of our knowledge. Its chemical stability towards H_2S (retention of the framework crystallinity and total H_2S adsorption capacity) was experimentally established by PXRD, SEM analyses and H_2S adsorption–desorption experimental cycles. *In situ* DRIFT experiments showed the formation of hydrogen bonds between H_2S molecules themselves confined in the pores of MIL-53(Al)-TDC, a small perturbation of the μ-OH group by H_2S and an overall weak H_2S adsorption within the pores of MIL-53(Al)-TDC. Molecular simulations provided us with the preferential adsorption sites for the H_2S molecules inside the channels of MIL-53(Al)-TDC and a moderate adsorption enthalpy for H_2S (-23.2 kJ mol^{-1}), and confirmed the regeneration viability of MIL-53(Al)-TDC, under mild conditions. A future step will be to consider the incorporation of this MOF into a polymer matrix to fabricate a hybrid mixed-matrix membrane that has been demonstrated as a viable process to capture H_2S in real conditions.[18]

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Conflicts of interest

There are no conflicts to declare.

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