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Article

Appending Polyamines on Metal–Organic Frameworks as an Efficient Strategy for Selective Removal of H_2S under Humid Conditions

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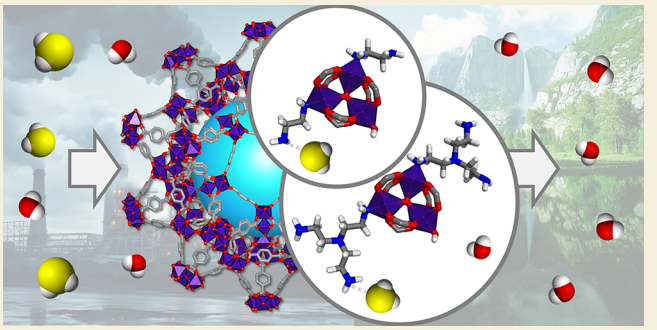
ABSTRACT: Removal of highly toxic and corrosive hydrogen sulfide from gas flows is of paramount importance for controlling the environment and in several industrial processes. This contribution reports a straightforward strategy to engineer sorbents for efficient hydrogen sulfide removal under humid conditions by functionalizing the open metal sites of metal–organic frameworks (MOFs) with polyamines. MIL-101(Cr) MOFs were successfully modified with ethylenediamine and tris(2-aminoethyl)amine, and the resulting materials were characterized using X-ray diffraction, FTIR, NMR, nitrogen sorption, and thermogravimetric analysis (TGA), confirming the functionalization. Although the functionalized MOFs exhibited a greater affinity for water compared to the unmodified MIL-101(Cr), they efficiently removed H_2S under humid conditions without framework degradation, whereas the pristine material did not. This was demonstrated by TGA-MS and elemental analysis and confirmed by density functional theory calculations. The developed approach offers a promising pathway for the design of advanced sorbents tailored for H_2S removal in industrial and environmental applications.



KEYWORDS: *metal–organic frameworks, postsynthetic functionalization, open metal site, amines, hydrogen sulfide*

INTRODUCTION

Hydrogen sulfide is a highly toxic and corrosive gas posing significant risks to human health, ecosystems, and infrastructure.[1−3] Its removal from gas streams is therefore crucial to comply with stringent environmental regulations and to ensure the preservation of industrial setups in various fields.[4−6]

In recent years, metal–organic frameworks (MOFs) have been shown to be promising materials for H_2S removal.[7−10] These materials consist of metal ions or clusters interconnected by organic linkers, which provides remarkable tunability and can lead to structures possessing high surface areas and a variety of chemical functionalities, making them attractive candidates for gas sorption and separation applications.[11−13] The removal of H_2S using MOFs so far primarily relies on the interactions between the gas molecules and the so-called open metal sites (OMSs) within the framework, which act as sorption sites.[14−16] The possibility to create OMSs in MOFs provides higher active site density compared to other materials, such as activated carbons and zeolites, resulting in improved gas capture efficiency.[17,18] OMSs are usually simply obtained by thermal removal of coordinated solvent molecules remaining from synthesis, often under a vacuum. However, those so-obtained sorption sites are prone to interact with any other guest molecules, which may pose selectivity issues.[19,20] In addition, H_2S adsorption toward OMSs can lead to partial destruction of the framework.[21,22] This is for example the case for the copper-based MOF HKUST-1 and has also been evidenced by the much more stable Fe-soc-MOF-1 and MIL-101(Cr).[8,16,21] The addition of functions of interest, such as amines, directly on the MOF linkers is another strategy that has been used with some success to enhance H_2S removal efficiency by providing more selective interaction sites.[23−25] However, this strategy involves the use of more expensive modified linkers. In both cases, the presence of moisture can lead to structural instability and/or less selective adsorption performance.[26,27]

The above-mentioned limitations highlight the need for developing new and cost-effective strategies to create stable MOF materials for efficient and selective hydrogen sulfide

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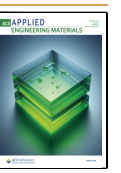

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removal. It should be noted, in addition, that reports on the H_2S sorption capacities of materials are limited, highlighting the need for safe experimental alternatives for the capture of such challenging toxic molecules.

Here, we propose an innovative and cost-effective approach to engineer MOFs for the removal of H_2S based on the functionalization of OMSs with polyamines (Figure 1). The use of polyamines prevents material degradation through direct and irreversible H_2S-to-metal binding by capping of the OMSs while also providing free amines for strong and selective reaction with H_2S without the need for modified linkers. This strategy was evaluated using the mesoporous MIL-101(Cr) (Figure 1A,B), selected for its mesoporosity, large surface area, and open metal sites, which are particularly favorable for functionalization with polyamines. Compared to other members of the MIL-101 family, the chromium derivative furthermore offers superior chemical stability, crucial for maintaining structural integrity during functionalization with amines and for removing H_2S in a humid atmosphere. Functionalization was achieved with ethylenediamine (EN) and tris(2-aminoethyl)amine (TREN) (Figure 1D,E).

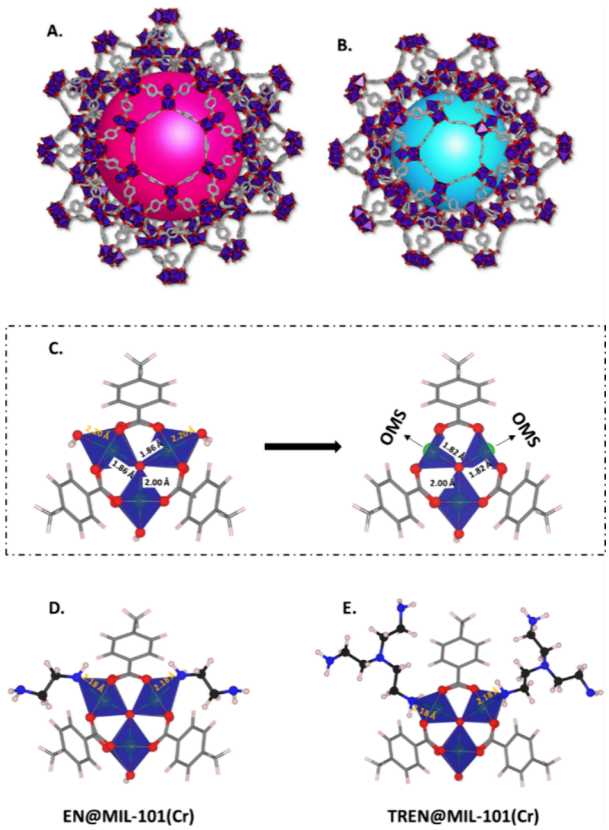

Figure 1. (A) Large and (B) small mesoporous cages of MIL-101(Cr) with (C) details of the cluster activation process for the removal of two coordinated water molecules, leading to the formation of two open metal sites (OMSs) per trinuclear cluster, while the third Cr remains coordinated to a charge-balancing anion, along with most stable coordination modes of the polyamines (D) EN and (E) TREN to the oxo-trimer as revealed by density functional theory calculations. Color code: purple, chromium; red, oxygen; gray, carbon; blue, nitrogen; white, hydrogen (H atoms were omitted for clarity in panels A and B).

We demonstrate that this approach is successful, showing high hydrogen sulfide adsorption selectivity against moisture without degradation of the material. We also provide a procedure to safely generate H_2S for materials testing in a closed environment, eliminating the need for handling pressurized cylinders.

RESULTS AND DISCUSSION

A single batch of MIL-101(Cr) was synthesized for further functionalization using a previously reported procedure.[28] The powder X-ray diffraction (PXRD) pattern, Fourier-transform infrared (FTIR) spectrum, and thermogravimetric analysis (TGA) of the obtained sample were in good agreement with data published earlier,[29,30] proving that it is composed of pure and highly crystalline MIL-101(Cr) (Figure 2A and Figures S3−S5). Nitrogen physisorption of the activated MOF revealed a Brunauer−Emmett−Teller (BET) specific surface area of 2964 ± 52 m^2/g, and pore size distribution analysis was performed according to the Barett−Joyner−Halenda (BJH) method showing the presence of two types of large pores (Figure 2B,C). It should be noted that although the BJH method gives underestimated pore sizes for materials with very small mesopores as is the case of MIL-101, it illustrates nicely their distribution pattern and enables comparison between similar materials. Those observations are all in line with previous reports.[31,32]

The postsynthetic functionalization of MIL-101(Cr) with polyamines was performed by activating the MOF and then refluxing it in a solution of the amine (TREN or EN) in toluene, followed by washing with appropriate solvents and drying (see the Supporting Information for details). The resulting functionalized MOFs are referred to as EN@MIL-101(Cr) and TREN@MIL-101(Cr). In the first attempts to synthesize TREN@MIL-101(Cr), methanol was used for washing. Despite the fact that it did not affect the crystallinity (see Figure S6), this resulted in incomplete functionalization due to a competition between TREN and methanol for the OMS positions, as revealed by ^1H NMR analysis of the digested MOF (see the Supporting Information for details). For the final syntheses, *n*-pentane was selected for washing owing to its ability to dissolve the amines while being noncoordinating to the OMSs. The PXRD patterns of EN@MIL-101(Cr) and TREN@MIL-101(Cr) washed with *n*-pentane (Figure 2A) present identical peak positions compared to unmodified MIL-101(Cr), proving that the crystallinity and framework structure were preserved. The changes of relative peak intensities are ascribed to the different electron densities of guest molecules in the pores.

The successful functionalization is further supported by the presence of overlapped signals at 1580 cm^{-1} (N−H bending) and 1275 cm^{-1} (C−N stretching) in the IR spectra of EN@MIL-101(Cr) and TREN@MIL-101(Cr) (Figure S7), absent in the spectrum of pristine MIL-101(Cr).[33,34] A broad band around 3000 cm^{-1}, corresponding to N−H stretching, is also present although quite weak. The number of amine ligands per cluster (Figure 1) in the functionalized MOFs was determined using solution ^1H NMR on samples digested in a NaOD/D_2O mixture (see the Supporting Information for details). This analysis shows that the grafting with ethylenediamine worked perfectly, leading to functionalization of the two available metal centers per cluster with a yield of 100%, while the functionalization with TREN led to a slightly lower functionalization yield of 94% (see Figure S8 and Table S1). The incomplete functionalization is likely due to the steric hindrance of TREN in comparison to EN. Elemental CHN

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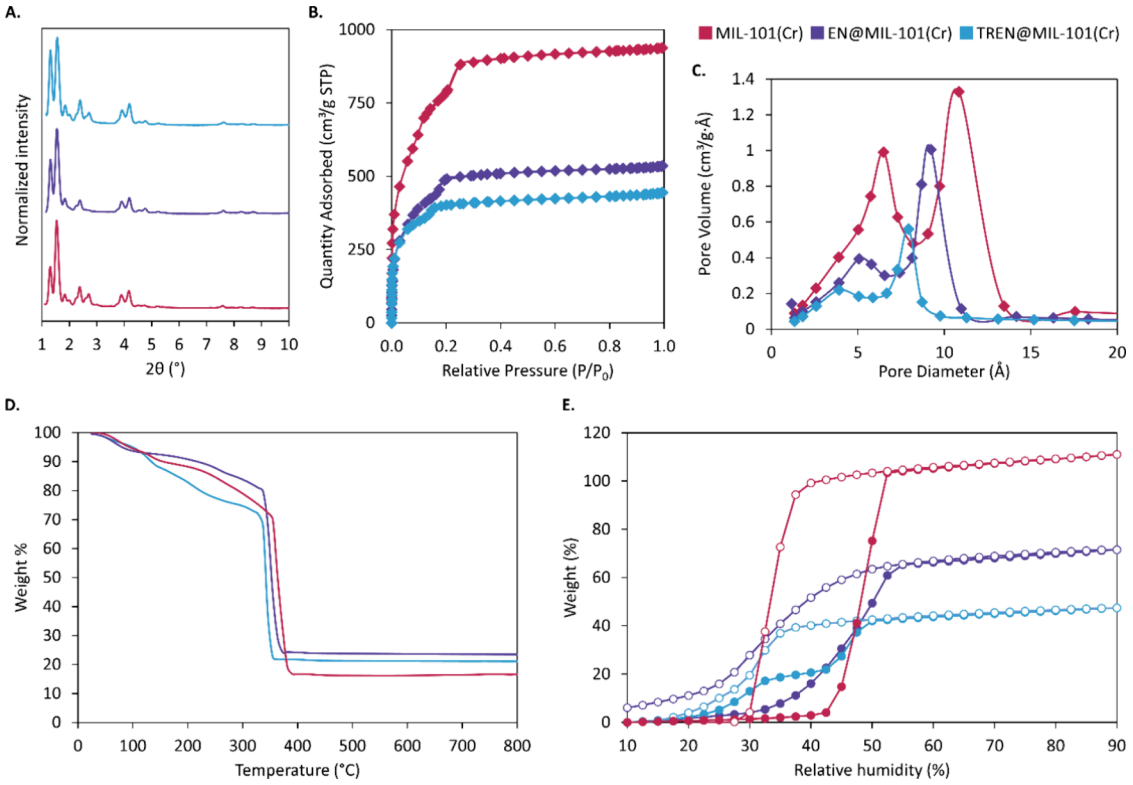

Figure 2. (A) PXRD patterns (λ = 0.71073 Å), (B) nitrogen sorption isotherms (77 K), (C) BJH pore size distributions, (D) thermogravimetric analyses under air, and (E) water adsorption isotherms of MIL-101(Cr) and its functionalized derivatives, EN@MIL-101(Cr) and TREN@MIL-101(Cr) (solid symbols, adsorption; empty symbols, desorption).

analysis further confirmed the successful functionalization of the two samples (Table S2).

The thermograms of pristine MIL-101(Cr) and the functionalized materials (Figure 2D) show similar behaviors, with gradual mass losses ranging from 20 to 30% below 350 °C, followed by the decomposition of the terephthalate linker at 350−375 °C. Calculations based on the results of the ^{1}H NMR characterization (Table S1) predict an ethylenediamine content of 15 wt % and a tris(2-aminoethyl)amine content of 29 wt % in the functionalized MOFs, which are smaller than the weight losses observed below the framework decomposition temperature. The remaining loss is thus attributed to water adsorbed from the atmosphere. Thermogravimetric analysis coupled to mass spectrometry (TGA-MS) (Figure S9) indicates that the polyamines remain grafted to the MOF at least up to a temperature of 100 °C. Heating to higher temperatures might lead to slow desorption of part of the amines, but no important decomposition coupled to CO_2 release is observed before reaching 200 °C.

Density functional theory (DFT) calculations were deployed to gain further understanding of the coordination of these amine functions on the activated MIL-101(Cr) OMSs. Various coordination modes were examined on the representative oxo-trimer clusters (Figure S14) and energetically compared (Figures S15 and S16). Our findings indicated that both polyamines (EN and TREN) preferentially bind the Cr^{3+} OMS via the nitrogen atoms of the $-NH_2$ groups, with a separating N−Cr distance of 2.18 Å (Figure 1D,E). The stability of these preferential settings was further revealed through ab initio molecular dynamics (AIMD) simulations performed at 300 K (see the Supporting Information for computational details). These calculations confirmed that the polyamines remain grafted to the Cr^{3+} OMSs via their nitrogen atoms, with only a slight shift observed in the separating Cr−N distances of 0.06 and 0.03 Å for EN and TREN, respectively.

Nitrogen sorption isotherms (Figure 2B) confirm an expected decrease in the BET specific surface area upon functionalization and a further decrease with increasing size of the amine, leading to still quite high surface areas of 1799 ± 46 m^2/g for EN@MIL-101(Cr) and 1423 ± 34 m^2/g for TREN@MIL-101(Cr). BJH analysis further reveals an expected decrease in pore size and volume with increasing size of the organic amine ligand (Figure 2C).

Prior to studying the removal of H_2S under humid conditions, the water uptake behavior of the materials was assessed by means of dynamic vapor sorption (DVS). The water sorption isotherm of MIL-101(Cr) (Figure 2E) reveals one adsorption step starting at approximately 42.5% of relative humidity (RH), corresponding to capillary condensation in the mesoporous cages, and resulting in a total mass increase of 111%, evidencing the significant water uptake capacity of this MOF. The desorption exhibits a hysteretic behavior, due to capillary condensation, with a sudden weight loss at 37.5% RH, in accordance with literature reports.[35,36] The water uptake observed here (1.11 g/g) is slightly higher than that previously reported (~0.9 g/g), correlating well with the higher BET specific surface area of our sample (2963 m^2/g) compared to the previously reported one (2500 m^2/g). EN@MIL-101(Cr) and TREN@MIL-101(Cr) present lower water uptakes (71 and 47 wt %, respectively) compared to pristine MIL-101(Cr), as part of the pore volume is taken up by the grafted amine molecules. Furthermore, the steep adsorption and desorption steps are shifted toward lower RH values, also due to the reduction of the pore size, leading to capillary condensation at

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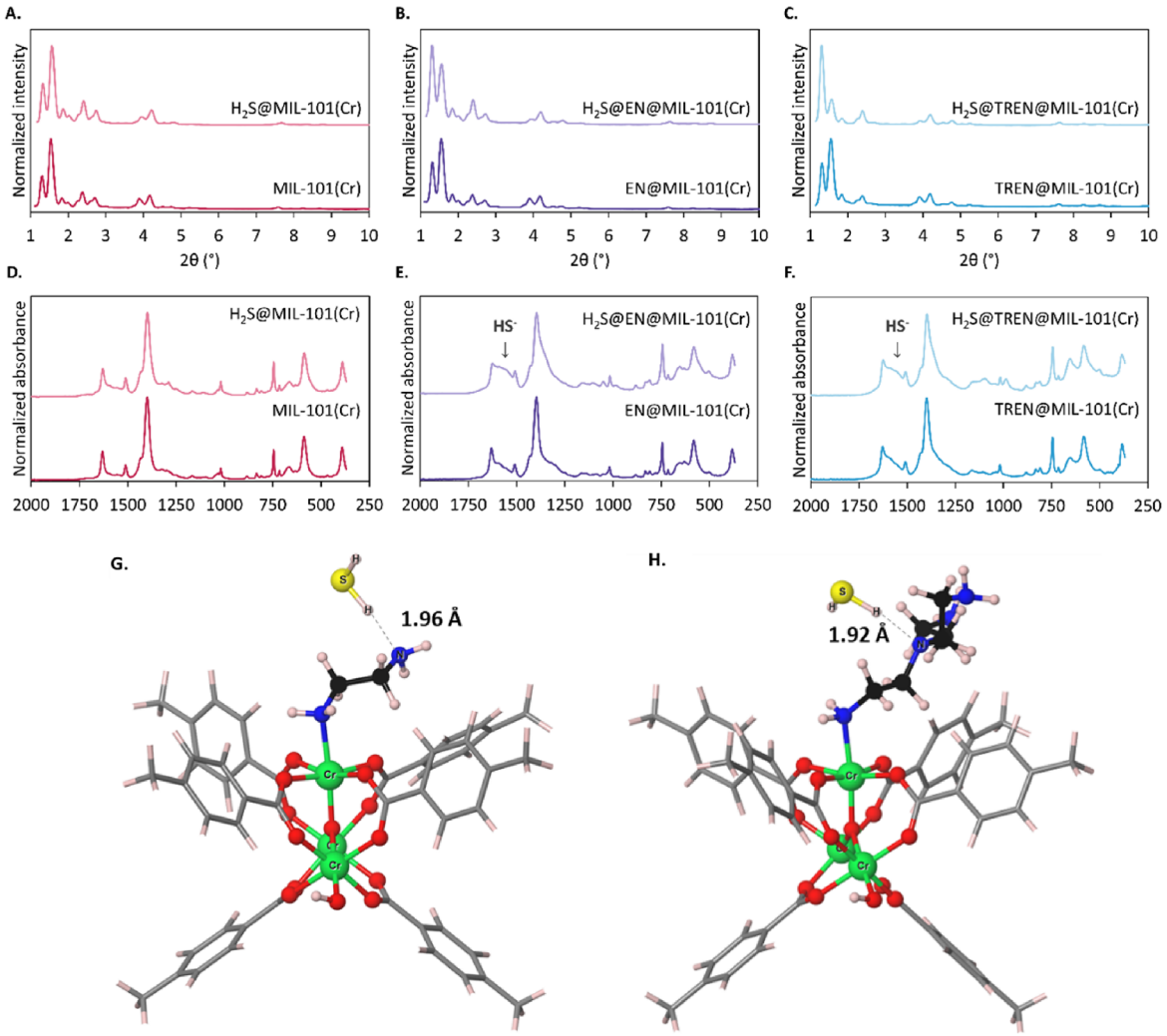

Figure 3. (A–C) PXRD patterns, (D–F) FTIR spectra of MIL-101(Cr), EN@MIL-101(Cr), and TREN@MIL-101(Cr) before and after H_2S sorption, and (G–I) DFT adsorption configurations of H_2S on EN@MIL 101(Cr) and TREN@MIL 101(Cr). Color code: green, chromium; gray, carbon; red, oxygen; white, hydrogen.

lower relative humidity. In contrast to pristine MIL-101(Cr) and EN@MIL-101(Cr), the TREN-functionalized MOF shows two distinct steps during the water uptake. This is likely because the TREN molecules take up space within the pores, leading to a marked contrast in the pore sizes between the small and large mesopores. The presence of free amines in the functionalized MOFs may also enhance the hydrophilicity of the internal surface, further decreasing the RH values at which adsorption of water occurs.[37] While the increased water uptake and hydrophilicity might suggest potential competition with H_2S sorption, the amine-functionalized MOFs are specifically designed to preferentially adsorb this gas even in the presence of moisture.

To evaluate the adsorption of H_2S by the pristine and amine-functionalized MIL-101(Cr) under safe conditions, the gas was first loaded into the MOFs and all characterizations were done ex situ. The gas was generated in an H-shaped tube containing $Na_2S{\cdot}9H_2O$ and the MOF sample in different branches (see the Supporting Information for the setup and details). Sulfuric acid was then injected on the sulfide to produce the desired gas under humid conditions, which is then adsorbed by the MOF. The H_2S-loaded MOF samples ("H_2S@MOF") were compared with SO_2-loaded samples ("SO_2@MOF" samples), obtained by using sodium metabisulfite instead of sodium sulfide in the H-shaped tube. For subsequent analyses, the synthesized samples were manipulated in a well-ventilated fumehood, enabling equilibration with atmospheric species, removal of nonspecifically bound H_2S or SO_2 molecules, and interaction with humidity from the air.

PXRD analysis was performed right after gas exposure and showed that all of the samples retained their structural integrity upon loading with both gases, with diffraction patterns displaying only variations in relative peak intensities (Figure 3A–C and Figure S10). FTIR spectroscopy reveals no differences between H_2S@MIL-101(Cr) and MIL-101(Cr) (Figure 3D,E). In contrast, a small new band at around 1550 cm^{-1}, overlapping with the signals of the framework, appears in the spectra of the amine-functionalized MOFs upon H_2S loading (Figure 3E,F). This is most probably assigned to the presence of hydrosulfides, formed by the acid–base reaction between H_2S and the dangling primary amines.

DFT calculations were performed on the oxo-trimer clusters (Figure 1D,E) loaded with 1 H_2S molecule. H_2S adsorbs similarly in both EN@MIL-101(Cr) and TREN@MIL-101(Cr), with resulting interaction energies of −33.5 and −35.4 kJ/mol, respectively. Examination of the optimized

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geometry unveiled that H_2S tends to form a hydrogen bond between its hydrogen atom and the unbound nitrogen of the polyamine EN and TREN molecules with separating distances of 1.96 and 1.92 Å, respectively (Figure 3H,I). Furthermore, an energetic comparison revealed that the detachment of polyamines by H_2S from the metal site is unfavorable.

Upon SO_2 sorption, the spectra of the amine-functionalized MOFs show the appearance of a signal at 1700 cm^{-1}, typical of C═O stretching of a carboxylic acid (Figure S11). This indicates the deterioration of MOFs in the presence of humid SO_2, likely due to the formation of H_2SO_3, followed by protonation of the carboxylates. The presence of a band at 1300 cm^{-1} indicates the presence of a S═O-containing species.

The release of volatile species upon heating the H_2S- and SO_2-loaded samples was evaluated by means of TGA-MS under a N_2 atmosphere (Figure 4 and Figure S12). The

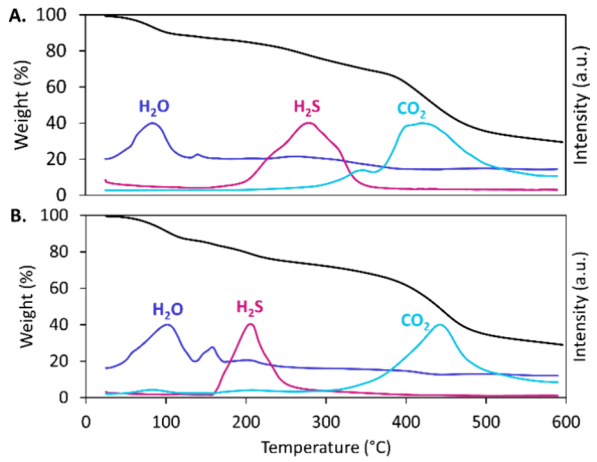

Figure 4. TGA-MS curves of H_2S@EN@MIL-101(Cr) and H_2S@TREN@MIL-101(Cr) with releases of water, hydrogen sulfide, and carbon dioxide (the latter being due to decomposition).

thermograms of the two H_2S@amine@MIL-101(Cr) MOFs (Figure 4) are very similar, up to a temperature of 100 °C, showing a mass loss of about 11%, corresponding to the release of water molecules. Between 100 and 340 °C, notable differences can however be observed in the trend of the TGA curves. MS analysis reveals that this is due to the temperature at which H_2S is released from the samples, peaking at 200 °C for the TREN-functionalized MOF and at 285 °C for the EN-functionalized one. Furthermore, the temperature range for the H_2S release from the EN-functionalized sample is much larger than for the TREN-functionalized one (i.e., 170 °C vs 100 °C). In both cases, the total mass loss due to H_2S departure is approximately 20%. The differences in the temperature at which hydrogen sulfide release occurs can be attributed to the fact that EN is more basic than TREN (pK_a EN = 10.7 and pK_a TREN = 10.0). The final weight loss, starting at 340 °C, corresponds to the release of CO_2 due to the decomposition of the framework.

In contrast, TGA-MS analysis of the SO_2-loaded samples (Figure S12) indicates that sulfur dioxide is not efficiently retained by the functionalized MOFs, and it is already released at around room temperature.

The contents of H_2S in H_2S@EN@MIL-101(Cr) and H_2S@TREN@MIL-101(Cr), determined from CHNS analysis, are found to be 12.8 and 11.3%, respectively (Table S3). It is worth noting that the amount of sorbed H_2S is close to the total amount of primary amines in each sample (with H_2S/$-NH_2$ ratios of 95% for EN and 83% for TREN). Nevertheless, as stated above, the DFT calculations indicate that this does not lead to decoordination of the polyamines from the metal sites as this scenario is not energetically viable. Replacing EN by TREN increases the amount of H_2S per polyamine (H_2S/EN mol % ratio: 1.9 and H_2S/TREN mol % ratio: 2.5), but it does not improve the gravimetric uptake of the material. This is due to the substantial increase in the molar mass when using the larger polyamine. Compared to other reported MOFs, the quantity of adsorbed H_2S is quite high, especially in the presence of usually strong competing guests, such as water (see Table S4 in the Supporting Information). However, it should be noted that a direct comparison with other materials is challenging, as different studies often employ varying experimental conditions for H_2S sorption, with many not accounting for the presence of competing molecules. In this work, the sorption was performed under humid conditions, which makes a direct comparison to studies conducted in dry environments or with different sorption methods not straightforward.

CONCLUSIONS

In summary, we demonstrated the successful synthesis and characterization of functionalized MIL-101(Cr) metal−organic frameworks with EN and TREN amines on open metal sites and the potential of the obtained materials for removal of H_2S in humid conditions. Coordination of two amine molecules on each Cr_3O cluster was achieved almost quantitatively. The surface areas and pore sizes of the functionalized MOFs were found to depend on the size and nature of the appended amines. Moreover, DVS analysis showed that the functionalized MOFs exhibited superior affinity for water compared to nonfunctionalized MIL-101(Cr), as evidenced by water uptake onsets at lower relative humidity, correlating with the smaller pore sizes determined by BJH analysis. The TREN- and EN-functionalized MOFs showed the efficient removal of H_2S under humid conditions. By contrast, in the presence of humidity, SO_2 was found to adsorb poorly and degrade the MOF. These findings suggest that postfunctionalization of MOFs with polyamines on metal sites is a promising approach for creating cost-effective and more stable sorbents for highly efficient specific separation and capture applications involving protic acidic gases.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaenm.4c00535.

Synthetic and gas loading procedures, description of instruments, PXRD patterns, FTIR spectra, TGA curves, NMR spectra, elemental analysis results, details of composition calculations, and DFT computational details (PDF)

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Notes

The authors declare no competing financial interest.

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