Zirconium and Aluminum MOFs for Low-Pressure SO₂ Adsorption and Potential Separation: Elucidating the Effect of Small Pores and NH₂ Groups

Philipp Brandt, Shang-Hua Xing, Jun Liang, Gülin Kurt, Alexander Nuhnen, Oliver Weingart,* and Christoph Janiak*

ABSTRACT: Finding new adsorbents for the desulfurization of flue gases is a challenging task but is of current interest, as even low SO₂ emissions impair the environment and health. Four Zr- and eight Al-MOFs (Zr-Fum, DUT-67(Zr), NU-1000, MOF-808, Al-Fum, MIL-53(Al), NH₂-MIL-53(Al), MIL-53(tdc)(Al), CAU-10-H, MIL-96(Al), MIL-100(Al), NH₂-MIL-101(Al)) were examined toward their SO₂ sorption capability. Pore sizes in the range of about 4–8 Å are optimal for SO₂ uptake in the low-pressure range (up to 0.1 bar). Pore widths that are only slightly larger than the kinetic diameter of 4.1 Å of the SO₂ molecules allow for multi-side-dispersive interactions, which translate into high affinity at low pressure. Frameworks NH₂-MIL-53(Al) and NH₂-MIL-101(Al) with an NH₂-group at the linker tend to show enhanced SO₂ affinity. Moreover, from single-gas adsorption isotherms, ideal adsorbed solution theory (IAST) selectivities toward binary SO₂/CO₂ gas mixtures were determined with selectivity values between 35 and 53 at a molar fraction of 0.01 SO₂ (10.000 ppm) and 1 bar for the frameworks Zr-Fum, MOF-808, NH₂-MIL-53(Al), and Al-Fum. Stability tests with exposure to dry SO₂ during ≤10 h and humid SO₂ during 5 h showed full retention of crystallinity and porosity for Zr-Fum and DUT-67(Zr). However, NU-1000, MOF-808, Al-Fum, MIL-53(tdc), CAU-10-H, and MIL-100(Al) exhibited ≥50–90% retained Brunauer–Emmett–Teller (BET)-surface area and pore volume; while NH₂-MIL-100(Al) and MIL-96(Al) demonstrated a major loss of porosity under dry SO₂ and MIL-53(Al) and NH₂-MIL-53(Al) under humid SO₂. SO₂ binding sites were revealed by density functional theory (DFT) simulation calculations with adsorption energies of −40 to −50 kJ·mol⁻¹ for Zr-Fum and Al-Fum and even above −50 kJ·mol⁻¹ for NH₂-MIL-53(Al), in agreement with the isosteric heat of adsorption near zero coverage (ΔHᵣ). The predominant, highest binding energy noncovalent binding modes in both Zr-Fum and Al-Fum feature μ-OH⁻−···SOO hydrogen bonding interactions. The small pores of Al-Fum allow the interaction of two μ-OH bridges from opposite pore walls with the same SO₂ molecule via OH⁻−···SOO⁻−···HO hydrogen bonds. For NH₂-MIL-53(Al), the DFT high-energy binding sites involve NH⁻−···SO together with the also present Al–μ-OH⁻−···SO hydrogen bonding interactions and C₆–π⁺−···NH₂, N–π⁺−···SO₂ interactions.

KEYWORDS: sulfur dioxide, pore size, adsorption, metal–organic framework, flue gas desulfurization

INTRODUCTION

A large fraction of the toxic gas sulfur dioxide (SO₂) is emitted into the atmosphere from industrial processes and fossil fuel combustion.¹ In 2018, energy-related coal combustion was accountable for 43% of SO₂ emissions worldwide.² SO₂ emissions are damaging to the biosphere both by forming acid rain and by contributing to air pollution issues, such as particulate matter (PM) with a diameter of ≤2.5 μm.³–⁵

Typically, wet limestone scrubbing or treatment by amine-based absorbents are used to remove SO₂ from flue gases. In both cases, the absorption is usually irreversible or accompanied by energy-intensive processes.⁶ Calcium sulfate is the product of limestone scrubbing and is oxidized to produce flue-gas-desulfurization (FGD) gypsum, which is mainly utilized in the construction industry. Yet, lime-stone scrubbing leaves up to 150–450 ppm of SO₂, which can significantly reduce other flue gas purification processes by inactivating sorbents for CO₂ removal or catalysts for selective reduction of NOₓ.⁷ On the other hand, reversible SO₂ adsorption could be utilized in a much fruitful way by aiming at producing the industrially crucial sulfuric acid, without other by-products.¹⁰ Dry FGD technol-
Oxidations are expected to become competitive if cycling-efficient adsorbents with quantitative SO\(_2\) removal would be available to balance the higher capital costs for a regeneration unit.\(^{11}\)

Metal–organic frameworks (MOFs) represent a promising adsorbent class due to record-holding surface areas (>7000 m\(^2\) g\(^{-1}\)) and uniform and designable porosity, typically in the microporous domain.\(^{12}\) A combination of both inorganic and...
organic building units is the reason for the high variety and tunability of MOF materials. Owing to their high porosity, MOFs outperform competing adsorbents, like zeolites and activated carbons, leading to a considerable number of studies related to various gas storage and gas separation applications, including the capture of toxic and polluting gases.

Until about 8 years ago, research on SO2 adsorption of MOFs was of specialized interest, but recently has experienced a surge of attention. For example, MFM-300(Al) and MFM-601(Zr) showed promising results for selective SO2 adsorption and outstanding robustness. Previous, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35 Previously, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35 Previously, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35 Previously, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35 Previously, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35 Previously, we had examined MIL-160(Al), which exhibited an excellent ideal adsorbed solution theory (IAST) selectivity of 128 at 293 K and 1 bar for SO2/CO2 gas mixtures.33-35

For the use of MOFs in the selective adsorption of SO2 traces below 500 ppm, the low pressure (p < 0.01 bar) SO2 uptake is more relevant compared to the overall capacity reached at ambient pressure. Currently, the designed synthesis of porous adsorbents for highly selective removal of SO2 from flue gas is still challenging and more endeavors are necessary to elucidate the underlying principles for optimal MOF SO2 adsorbents. A model of potential factors influencing the selective SO2 adsorption of an adsorbent is visualized in Figure 1.

So far, it is still a matter of discussion as to which factors constitute high SO2 uptakes at low pressures (p < 0.01 bar). In this work, we elucidate small pore widths and NH2-substituents as critical MOF parameters to achieve high quantities in low-pressure SO2 adsorption by focusing on Al- and Zr-MOFs, which are generally regarded as rather hydrothermally stable. Also the determination of IAST-selectivities for SO2/CO2 gas mixtures provides a first indication for the separation performance of a given material. Overall, the results should allow designing MOFs to remove low SO2 concentrations from N2/CO2/SO2 gas mixtures.

**RESULTS AND DISCUSSION**

Four Zr- and eight Al-MOFs were investigated in this work and are presented in Scheme 1. Structural details are given in Section S2. The SO2 sorption isotherms of these 12 MOFs were measured volumetrically up to 0.96 bar at 293 K. For clarity in the presentation of the SO2 sorption isotherm diagrams, we will discuss Zr-MOFs and Al-MOFs separately.

**SO2 Adsorption by Zr-MOFs.** All of the four representative Zr-MOFs have Zr6 nodes albeit with different ligand connectivity numbers of 12, 8, or 6 for Zr-Fum, DUT-67(Zr), and NU-1000 or MOF-808, respectively.

Zr-fumarate (Zr-Fum) shows a good SO2 affinity, already at 0.11 bar, with an SO2 uptake of 3.1 mmol·g⁻¹, which increases to a maximum of 4.9 mmol·g⁻¹ at 1 bar (Figure 2). MOF-808 and DUT-67(Zr) both exhibit two-step SO2 adsorption isotherms (Figure 2a). In MOF-808, the first adsorption step finishes at 0.01 bar with an SO2 uptake of 2.1 mmol·g⁻¹, followed by a moderate uptake in the pressure range of 0.01–0.5 bar up to 8.8 mmol·g⁻¹. The second step ends at 0.6 bar with an SO2 uptake of 12.7 mmol·g⁻¹, followed by a saturation stage with a maximum of 14.6 mmol·g⁻¹ at 1 bar. Both DUT-67(Zr) and Zr-MOF NU-1000 exhibit moderate SO2 adsorption capabilities in the low-pressure range with SO2 uptakes of 0.7 and 0.6 mmol·g⁻¹ at 0.01 bar as well as 2.3 and 2.6

**EXPERIMENTAL SECTION**

**Materials and Methods.** All reagents were purchased from commercial vendors and used without further purification. The MOFs were synthesized according to the published literature or were purchased (Table S1). The MOF identity was established by positively matching the powder X-ray diffraction (PXRD) with the simulation (PXRD) measurements were performed on a Bruker D2 Phaser with a Cu Kθ-cathode source (λ = 1.54182; 30 kV, 10 mA) at room temperature. The finely ground samples were measured in the 5° < 2θ < 50° range at a scan rate of 40° s⁻¹ using a flat, low background silicon sample holder. N2 gas adsorption for the Brunauer–Emmett–Teller (BET) surface area and porosity characterization was performed on a Quantachrome Autosorb iQ MP.

Before each gas sorption experiment, the samples were activated according to the literature (≤3 h of degassing at ≤393 K and a ~5 × 10⁻³ mbar vacuum). The gases (He, N2, SO2, CO2) were of ultrahigh purity (99.999%). The standard temperature and pressure (STP) volumes at 293.15 K and 101.325 kPa are reported in all cases according to the recommendation of the National Institute of Standards and Technology (NIST). The N2 adsorption experiments were performed within a pressure range of 0.005–1 bar at 77 K, the SO2 sorption experiments from 0.001 to 1 bar (0.95 ± 0.007 bar) at 293 K, and CO2 sorption experiments from 0.001 to 1 bar (0.95 ± 0.005 bar). A Dräger Pac 6000 electrochemical SO2 sensor with a measuring range of 0.1–100 ppm was used for leakage testing and maintaining safe work conditions.

**Figure 2.** SO2 sorption isotherms (293 K) of examined Zr-MOFs: (a) 0.001–1 bar and (b) 0.001–0.12 bar.
mmol·g⁻¹ at 0.1 bar, respectively (Table 1). DUT-67(Zr) shows a slight adsorption step at ~0.3 bar and a further increase until a maximum SO₂ uptake of 9.0 mmol·g⁻¹. The SO₂ adsorption isotherm of NU-1000 increases rather steadily with a maximum SO₂ uptake of 12.2 mmol·g⁻¹ at 1 bar and 293 K (in agreement with the isotherm in ref 52). The saturation uptake could not be reached in NU-1000 due to its micro- and mesoporosity with pore diameters of ~12 and ~29 Å for the triangular and hexagonal pore cross sections, respectively. 43 Although all four Zr-MOFs have a bi- or multimodal pore size distribution (Table 1), we assign the observation of a two-step SO₂ adsorption in MOF-808 and DUT-67 to the simultaneous smaller (4.8 and 8.8 Å) and larger (16.6 and 18.4 Å) micropore diameters in the frameworks. 42 The two MOFs, Zr-Fum and MOF-808, with a significantly higher low-pressure uptake feature an equally smallest pore width (both 4.8 Å). The smaller pore width of DUT-67(Zr) is 8.8 Å and that of NU-1000 is 12 Å. 42 For a high low-pressure SO₂ adsorption, this suggests an optimal pore diameter of ~4 to <8 Å, as will be further discussed in the Porosity–Adsorption Relationships section.

Table 1. Characteristics of Examined Materials in this Work and the Results of SO₂ Adsorption at 293 K

<table>
<thead>
<tr>
<th>material</th>
<th>BET-surface area[d] [m²·g⁻¹]</th>
<th>total pore volume[d] [cm³·g⁻¹]</th>
<th>pore width[d] [Å]</th>
<th>SO₂ uptake [mmol·g⁻¹] at</th>
<th>SO₂/CO₂ IAST selectivity[d] at SO₂/CO₂ molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Fum</td>
<td>600</td>
<td>0.290</td>
<td>4.8; 5.6; 7.4 ⁴⁴</td>
<td>1.2</td>
<td>3.1</td>
</tr>
<tr>
<td>MOF-808</td>
<td>1990</td>
<td>0.749</td>
<td>4.8; 18.4 ⁴⁵</td>
<td>2.1</td>
<td>3.6</td>
</tr>
<tr>
<td>DUT-67(Zr)</td>
<td>1260</td>
<td>0.544</td>
<td>8.8; 16.6 ⁴⁶</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>NU-1000</td>
<td>1740</td>
<td>1.196</td>
<td>12; 29 ⁴⁵</td>
<td>0.6</td>
<td>2.6</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>1450</td>
<td>0.706</td>
<td>8.5 ⁴⁶</td>
<td>0.4</td>
<td>3.3</td>
</tr>
<tr>
<td>NH₂-MIL-53(Al)</td>
<td>620</td>
<td>0.358</td>
<td>7.3 ⁴⁵</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Al-Fum</td>
<td>970</td>
<td>0.447</td>
<td>5.8 ⁴⁶</td>
<td>1.0</td>
<td>4.1</td>
</tr>
<tr>
<td>MIL-53(μc)(Al)</td>
<td>1000</td>
<td>0.415</td>
<td>8 ⁴⁶</td>
<td>0.6</td>
<td>5.0</td>
</tr>
<tr>
<td>CAU-10-H</td>
<td>600</td>
<td>0.258</td>
<td>6 ⁴⁶</td>
<td>1.2</td>
<td>3.7</td>
</tr>
<tr>
<td>MIL-96(Al)</td>
<td>530</td>
<td>0.237</td>
<td>~4; ~11 ⁴⁵</td>
<td>1.2</td>
<td>3.7</td>
</tr>
<tr>
<td>MIL-100(Al)</td>
<td>1890</td>
<td>0.824</td>
<td>25; 29 ⁴⁵</td>
<td>0.4</td>
<td>2.5</td>
</tr>
<tr>
<td>NH₂-MIL-101(Al)</td>
<td>1770</td>
<td>1.001</td>
<td>25; 34 ⁴⁵</td>
<td>1.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

[a] Ideal adsorbed solution theory (IAST) selectivity at 1 bar. See Section S4 for the CO₂ sorption data. [b] BET surface areas were calculated from five adsorption points of N₂ adsorption isotherm data within 0.05 < p/p⁰ < 0.2. Values were rounded with the estimated standard deviation ± 50 m²·g⁻¹. Total pore volumes were calculated from the experimental N₂ sorption data at 0.85 < p/p⁰ < 0.95, depending on the isotherm shape. For details, see Section S3.3. [c] Pore widths as given in the literature. [d] Large pore form.

Figure 3. SO₂ sorption isotherms (293 K) of examined Al-MOFs: (a–c) 0.001–1 bar and (d–f) 0.001–0.11 bar.

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The Al-MOFs, MIL-53(Al), NH2-MIL-53(Al), Al-Fum, MIL-53(tdc)(Al), and CAU-10-H, have one-dimensional channels with nearly square to rhombic cross sections of 5.8–8.5 Å. MIL-53(Al) and NH2-MIL-53(Al) differ from the other MOFs by their reversible breathing behavior with the adsorption of guest molecules.\(^{44,54}\) The complex structure of MIL-96(Al) consists of an isolated, not accessible pore A and “zig-zag” channels connecting the larger B and the smaller pore C.\(^{49,55}\) MIL-100(Al) and NH2-MIL-101(Al) have 3D pore networks of spherical mesopores of diameter ≥25 Å connected by smaller windows.

The SO2 adsorption isotherms of MIL-53(Al) and NH2-MIL-53(Al) (Figure 3a,d) show SO2 uptakes to 3.3 and 4.3 mmol g\(^{-1}\), respectively, at 0.1 bar, which is followed by a flattening of the adsorption. Noteworthy is the rather steep increase for NH2-MIL-53(Al) respectively, at 0.1 bar, which is followed by a.

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The amino-functionalized MOF NH2-MIL-101(Al) shows an initial steep increase up to ~0.01 bar, very similar to NH2-MIL-53(Al) (Figure 3d,f). An enhanced SO2 uptake at low pressures was seen with amino functionalization for both NH2-MIL-53(Al) and NH2-MIL-101(Al) compared to their closely related frameworks, MIL-53(Al) and MIL-100(Al), respectively (Figure 3c,f). This early increase in uptake of the two NH2-functionalized MOFs is much steeper than what is seen in this pressure range for the other Al-MOFs (cf. Figure 3d–f), which suggests its origin in the NH2 group. This is in agreement with similar observations for the MOFs NH2-MIL-125(Ti)\(^{59}\) and also coincides with findings for NH2-Uio-66 exhibiting higher heat of adsorption values near zero coverage and a higher SO2/CO2 selectivity, compared to the parent Uio-66.\(^{60}\) From a simulation of mmen-MIL-101(Cr) (mmen = N\(_2\)N'-dimethylethylenediamine), the SO2 adsorption sites were found to be transferred from Cr(III) in MIL-101(Cr) to the NH amino groups.

The lone-pair electrons from N interact with the S(\(SO_2\)) atom that has a partial positive charge. The mmen-NH groups form hydrogen bonds to O(\(SO_2\)) of the same SO2 molecule, with distances of 1.92 and 2.27 Å as the predominant adsorption site.\(^{62}\)

One gram of NH2-MIL-53(Al) and NH2-MIL-101(Al) corresponds to 4.5 or 4.5 mmol of the formula unit, respectively (cf. formula unit in Scheme 1) or to 4.5 mmol NH2-bdc. Thus, at 0.01 bar, when the SO2 uptake slope decreases, the ratios are ~2 SO2/4.5 NH2-bdc in NH2-MIL-53(Al) and ~1.5 SO2/4.5 NH2-bdc in NH2-MIL-101(Al). This suggests that two adjacent NH2-groups can bind one SO2 through two NH···OSO···HN hydrogen bonds in a high-affinity site. For NH2-MIL-101(Al), the SO2 uptake passes 3.6 mmol g\(^{-1}\) at 0.1 bar and continues with relatively steady adsorption and reaches, albeit at no saturation yet, a maximum uptake of 17.3 mmol g\(^{-1}\) at 1 bar, which is one of the highest reported in the literature (for a comprehensive compilation of literature data regarding SO2 adsorption in MOFs, see Table S8). Ibarra et al. have recently investigated SO2 adsorption in MIL-101(Cr) in which the bdc ligand was partially substituted with tetrafluoro-1,4-benzenedi-carboxylate (4F-bdc) and showed a roughly similar isotherm shape to the isoreticular NH2-MIL-101(Al) but with slightly higher SO2 adsorption capacity with SO2 uptakes of 4.6 and 18.4 mmol g\(^{-1}\) at 0.1 bar and 1 bar, respectively, at 298 K and featured exceptional stability against SO2.\(^{62}\)

We do not see an effect of aqua ligands at the SBU for an enhanced SO2 uptake at low pressure since MIL-100(Al) and NH2-MIL-101(Al) with the same \{Al\((\mu_2-O)(OH)\)-(H\(_2\)O)\(_2\)(O\(_2\)C\(_2\))\(_3\)\} SBU behave quite differently (Figure 3f). The former has the lowest SO2 uptake of up to 0.1 bar of all Al-MOFs. This is not to say that there would be no effect of aqua ligands or adsorbed water for other things being equal.

Ibarra et al. could observe enhanced SO2 adsorption in the MFM-300 series related to small amounts of pre-absorbed EtOH.\(^{28}\) Also, Li et al. predicted enhanced SO2 adsorption for MIL-160 with 0.3% pre-absorbed water.\(^{53}\)
The terminal metal-OH and metal-bridging $\mu_\delta$-OH-groups can also significantly contribute to the SO$_2$ adsorption performance since these groups enter in hydrogen bonding/electrostatic interactions with SO$_2$ ($\text{M-O}^\delta\cdots\text{H}^\delta\cdots\text{O}^\delta\cdots\text{S}^\delta\cdots\text{O}^\delta\cdots$)\textsuperscript{28,33,36,62} In our chosen Zr- and Al-MOFs, all examples feature these OH groups. In situ inelastic neutron scattering and density functional theory (DFT) calculations on the SO$_2$ adsorption in MFM-300(Al)\textsuperscript{33} and in situ synchrotron PXRD studies for SO$_2$ in MFM-601(Zr)\textsuperscript{64} revealed metal-OH···O=S=O hydrogen bonds for the first adsorbed SO$_2$ molecules. Other than that, the effect of $\mu$-OH-groups regarding SO$_2$ adsorption is rarely examined in the literature. In the DFT Calculations section, we present potential binding sites of SO$_2$ in the representative MOFs, Zr-Fum and Al-Fum, which affirm the significant contribution of metal-OH···O=S=O interactions.

**Porosity–Adsorption Relationships.** The accessible surface area and the total accessible pore volume are often taken as the two prime MOF characteristics governing gas adsorption. Plots of the SO$_2$ uptake at 1 bar against the BET-surface area and total pore volume (Figure 4a,b) show a reasonably linear correlation for most MOFs. Noteworthy outliers in the surface area correlation are NH$_2$-MIL-101(Al), MIL-100(Al), and NH$_2$-MIL-53(Al) with a higher than expected uptake based on the surface area. For NH$_2$-MIL-101(Al) and MIL-100(Al), their high total pore volume from micro- and mesopes gives rise to the higher uptake. The higher than expected SO$_2$ uptake for the flexible MOF, NH$_2$-MIL-53(Al), may be traced to a different extent of breathing with SO$_2$ at 293 K and N$_2$ at 77 K (where the latter yielded the accessible surface area and pore volume).

An outlier to significantly lower uptake in the uptake–pore volume relation is the Zr-MOF NU-1000, which has the highest total pore volume, even more than MIL-100(Al) and NH$_2$-MIL-101(Al), and is predominantly mesoporous. N$_2$ sorption studies with t-plot analysis yielded micro-to-total pore volume ratios (cm$^3$ g$^{-1}$/cm$^3$ g$^{-1}$) of 0.21/1.20 for NU-1000, 0.55/0.82 for MIL-100(Al), and 0.61/1.00 for NH$_2$-MIL-101(Al) (Table S2). The total pore volume represents a limit for the maximum capacity but the SO$_2$ adsorption isotherm of NU-1000 at 1 bar still has a high positive slope and is far from leveling off, which indicates an adsorption curve far from saturation, which will be reached only at higher pressures. Evidently, a primarily mesoporous material can be positioned below the linear trend line of the uptake–total pore volume dependence.

However, flue gas desulfurization or SO$_2$ gas sensors operate at low partial pressures of SO$_2$. When it comes to the desired high uptake at low pressure, there is no longer a surface area or total pore volume correlation. The low-pressure uptake at 0.01 and 0.1 bar is clearly independent of surface area (Figure S35). Instead, the uptake and isotherm characteristics in the low-pressure region (Figure S34) must be correlated with the SO$_2$ affinity of the materials. By fitting the SO$_2$ adsorption isotherms with an appropriate model, the affinity constants can be obtained (Table S3 and Figures S39–S50). A high-affinity constant between the adsorbent and the adsorbate reflects a high gas uptake at low pressure, which is a type-I isotherm.

When the surface-specific SO$_2$ uptake, that is, the uptake at low pressures (0.01 and 0.1 bar) divided by the BET-surface area, is plotted against the pore limiting diameter (PLD), an obvious maximum is obtained (Figure 5). The surface-specific SO$_2$ uptake is obtained by normalization, i.e., division of the uptake through the surface area, which is necessary as the absolute value of the uptake at low pressure depends on the available surface area. The PLD is defined as the smallest diameter of a pore or pore window in a framework. The maximum of low-pressure uptake vs PLD suggests an optimal pore diameter in the range between $\sim$4 and 8 Å.\textsuperscript{30} The value of 4 Å agrees with the kinetic diameter of SO$_2$ (4.1 Å).\textsuperscript{48} In this PLD range, one can assume the SO$_2$ molecule to have dispersive interactions with both ends of the molecule to the surface. Such local optima are known for adsorbent structures where the opposite Connolly surfaces are at a distance of the length of the

![Figure 4](https://example.com/fig4.png)  
*Figure 4. SO$_2$ uptake (1 bar, 293 K) vs (a) BET-surface area and (b) total pore volume. The dashed line is a trend line as a guide to the eye.*

![Figure 5](https://example.com/fig5.png)  
*Figure 5. Surface-specific SO$_2$ uptake at 0.1 bar (293 K), which is the uptake at this pressure divided by the BET-surface area vs the pore limiting diameter (PLD). See Figure S36 for the surface-specific SO$_2$ uptake at 0.01 bar.*
adsorbed molecule, which can then simultaneously interact with the accessible surface at its opposite sides.\textsuperscript{57} Grand-canonical-Monte Carlo (GCMC) simulations for a series of small-pore MOFs have shown a good correlation between the SO\textsubscript{2} uptake at reduced pressures (0.05 bar) and the heat of adsorption.\textsuperscript{66}

A pore width of \(\sim 4\ \text{Å}\) between the Connolly surfaces, i.e., the distance between probe-accessible surfaces of the opposite pore sides\textsuperscript{57} allows the SO\textsubscript{2} molecule to have optimal multi-side dispersive interactions. The optimum range up to \(\sim 8\ \text{Å} = 2 \times 4\ \text{Å}\) can be rationalized through the side-by-side interactions of two adjacent SO\textsubscript{2} molecules through (framework-)O\(=\cdots\text{O} = \text{S} = \text{O} = \text{O}\)-(framework) dipole–dipole interactions. The drop in the surface-specific uptake at larger pore sizes above 8 Å is then due to a change to “one-sided” interactions for the adsorbed SO\textsubscript{2} molecules with the uptake of further SO\textsubscript{2} molecules occurring solely through (framework-)O\(=\cdots\text{O} = \text{S} = \text{O}\) dipole–dipole interactions.\textsuperscript{67} MOF-808 shows a somewhat low surface-specific SO\textsubscript{2} uptake at 0.1 bar, but, at an even smaller pressure of 0.01 bar, it has comparable good performance as Al-Fum (Figure S36).

From the conclusion that SO\textsubscript{2} will be preferentially adsorbed in the smallest pores at low pressures, one can also assume the micropore volume or the micropore surface area as the normalizing denominator for the surface-specific SO\textsubscript{2} uptake vs the PLD. The micropore surface area normalization is given in Figures S37 and S38 (at 0.1 and 0.01 bar, respectively). This SO\textsubscript{2} uptake normalization, however, then overenhances the uptake of the two amino-functionalized MOFs, NH\textsubscript{2}-MIL-53(Al) and NH\textsubscript{2}-MIL-101(Al). Thereby, the importance of amino groups is demonstrated at the same time. Yet, the very small micropore surface area of the largely mesoporous NH\textsubscript{2}-MIL-101(Al) gives a small value in the denominator upon normalization, which together with the high uptake of NH\textsubscript{2}-MIL-101(Al) then leads to an overall high SO\textsubscript{2} uptake even with the large PLD of about 25 Å (Figures S37 and S38). This would distort the conclusions drawn with respect to PLD.

In summary, the SO\textsubscript{2} adsorption isotherms of typical Zr- and Al-MOFs (Figures 2 and 3 for a combination, see Figure S34) show a wide range of shapes and uptake values in the relevant pressure regions. Once again, we note that a total SO\textsubscript{2} uptake at 1 bar, here found between \(\sim 5\) and 17 mmol g\textsuperscript{-1} at 293 K, is less meaningful when aiming for an application in SO\textsubscript{2} separation to an overall high SO\textsubscript{2} uptake even with the large PLD of about 25 Å (Figures S37 and S38). This would distort the conclusions drawn with respect to PLD.

**IAST Selectivity.** The ideal adsorbed solution theory (IAST) model is a method that gives first estimations on the mixed gas adsorption behavior of an adsorbent based on data gained from single-gas adsorption experiments. IAST-based estimations are most suitable when the following conditions are fulfilled: (i) the same accessible surface area is available to all adsorbates, (ii) low pressures (\(\leq 1\) bar), and (iii) similar polarity of adsorbates.\textsuperscript{68} IAST selectivities in this work were calculated with the “3P sim” software (see the Supporting Information) by fitting the adsorption isotherm data points with the dual-site Langmuir Sips model (DSLS) (Figures S39–S50). Parameters are given in Table S2.

CO\textsubscript{2} can be regarded as the main competitor to SO\textsubscript{2} for a potential adsorptive separation during flue gas desulfurization. IAST selectivities for SO\textsubscript{2}/CO\textsubscript{2} gas mixtures for selected MOFs are displayed in Figure 6 (see Table 1 and Figure S51 for all MOFs).

The highest calculated SO\textsubscript{2}/CO\textsubscript{2} IAST selectivities at 1 bar and low SO\textsubscript{2} mol fraction of 0.01 (1% or 10.000 ppm SO\textsubscript{2}) were 53, 48, 41, and 34 for Zr-Fum, MOF-808, NH\textsubscript{2}-MIL-53(Al), and Al-Fum, respectively (Table 1). These MOFs had all shown an early steep SO\textsubscript{2} uptake (Figures 2b and 3d), which is one understandable prerequisite for a high SO\textsubscript{2}/CO\textsubscript{2} IAST selectivity at a low molar fraction of SO\textsubscript{2} together with a low CO\textsubscript{2} uptake at low pressure (see Table S4).

**Isosteric Enthalpy of Adsorption.** The isosteric enthalpy of adsorption (\(\Delta H_{\text{ads}}\)) for SO\textsubscript{2} was determined for the representative MOFs, Zr-Fum, Al-Fum, and NH\textsubscript{2}-MIL-53(Al), by applying a virial analysis on adsorption isotherm data measured between 293 and 303 K (Figure 7; for details see Section S6.2). The isosteric enthalpy of adsorption near zero coverage (\(\Delta H_{\text{ads}}^{0}\)) in Zr-Fum is \(-49\ \text{kJ mol}^{-1}\), whereas Al-Fum and NH\textsubscript{2}-MIL-53(Al) exhibit values of \(-42\) and \(-67\ \text{kJ mol}^{-1}\), respectively. At maximum loading, \(\Delta H_{\text{ads}}\) decreases to \(-16\), \(-30\), and \(-58\ \text{kJ mol}^{-1}\) for Zr-Fum, Al-Fum, and NH\textsubscript{2}-MIL-53(Al), respectively. The values of \(\Delta H_{\text{ads}}^{0}\) can be compared with the DFT-calculated highest binding energies (see below). For Zr-Fum and Al-Fum, the \(\Delta H_{\text{ads}}^{0}\) value is of the same order of magnitude as in the previously investigated Zr-MOFs (\(-48\) and \(-51\ \text{kJ mol}^{-1}\) for MFM-600\textsuperscript{64} and NU-1000,\textsuperscript{52} respectively) and Al-MOFs (\(-42\) and \(-42.8\ \text{kJ mol}^{-1}\) for MIL-160\textsuperscript{36} and CAU-10-H,\textsuperscript{58} respectively). The overall higher adsorption enthalpy for NH\textsubscript{2}-MIL-53(Al) can be explained by the strong interaction of the amino group with the polarizable SO\textsubscript{2} molecule.

![Figure 6](https://acsami.org/)
Moreover, we note that the distinction between framework must endure harsh conditions of humid SO2, containing the many of them degrade when moisture is present.59 Also, the presence of water could partially shift the adsorption of SO2 after dry or humid SO2 exposure, were rarely observed. More primary quantitative parameters (Figures S22 and the total pore volume after exposure were used as the examined qualitatively, while changes of the BET-surface area signiﬁcantly and indicative of framework degradation were losses for some MOFs. Hence, a combination of diﬀraction and adsorption experiments is always recommended. Moreover, we note that the distinction between framework degradation and irreversible adsorption is not trivial. However, in materials with potential applicability for FGD, neither framework degradation nor irreversible SO2 adsorption is preferable. An overview of the results from BET-surface analyses and accessible pore volume, by relating treated/pristine samples, is presented in Figure 8.

Under dry SO2 exposure, NH2-MIL-100(Al) and MIL-96(Al) had already demonstrated a major loss of porosity, and thus were deemed SO2-unstable. Interestingly, the dry SO2 exposure during ≤10 h did not strongly aﬀect the majority of examined materials (≥90% retained BET-surface area and pore volume). In contrast, under humid SO2 exposure during 5 h, most MOFs showed a noticeable decrease in accessible porosity. After humid SO2 exposure, the surface areas of MIL-53(Al) and NH2-MIL-53(Al) decreased by more than 50%, while NU-1000, MOF-808, Al-Fum, MIL-53(tdc), CAU-10-H, and MIL-100(Al) showed less signiﬁcant losses in surface area (≥50–90% retained BET-surface area and pore volume). Only Zr-Fum and DUT-67(Zr) showed good performance in both stability tests without a noticeable decrease in porosity. Both MOFs previously showed good water stability also under acidic conditions.40,69

DFT Calculations. For the investigation and illustration of the possible binding sites of SO2 we applied dispersion-corrected DFT (DFT-D) calculations on model frameworks of the three example MOFs—Zr-Fum, Al-Fum, and NH2-MIL-53(Al). Distances between the oxygen atom of the SO2 molecule and hydrogen atoms of the framework above 2.8 Å were not viewed as (O/C=–H···O bonds, as the distances between the SO2 sulfur atom and oxygen atoms of the MOF were above 4 Å. For computational details, see Section S7.

Zr-Fum. With the discrete secondary building units in Zr-Fum, a cluster approach is appropriate. To mimic the local pore environment in Zr-Fum, three diﬀerent cluster models, each being neutral, were isolated from its crystal structure (Figure 9).

Hydroxido-Centered Model 1. An isolated \([Zr_6(\mu_3-O)(\mu_4-OH)(Hfum)]_2(O_2CH)_9\) cluster with three mono-deprotonated fumarate\(^{1-}\) ligands surrounding a \(\mu_3-OH\) group by spanning the three edges of a triangular face of the Zr\(6\) octahedron was used to model part of the pore cavity (Figure 9a). Out of the 12 bridging fumarate\(^{2-}\)ligands around a Zr\(6\) cluster in Zr-Fum, nine ligands were replaced by formate ligands, \(O_2CH\), each spanning a Zr···Zr edge of the Zr\(6\) octahedron. This ensured the electroneutrality of the cluster model.

Metal-Centered Model 2. An isolated \([Zr_6(\mu_3-O)(\mu_4-OH)(Hfum)]_2(O_2CH)_9\) cluster with four fumarate\(^{1-}\)ligands surrounding a metal vertex by spanning the four edges around a Zr corner of the Zr\(6\) octahedron was used (Figure 9b).

Oxido-Centered Model 3. The \([Zr_6(\mu_3-O)(\mu_4-OH)(Hfum)]_2(O_2CH)_9\) cluster is similar to model 1, except that the three fumarate\(^{1-}\)ligands now surround a \(\mu_3-O\) group (Figure 9c,d).

Four main binding sites for SO2 are found in the optimized cluster models of Zr-Fum (Figure 9). In binding site 1 of the hydroxo-centered model 1, the O atom of SO2 interacts with the H atom of the \(\mu_3-OH\) group. This \(OH^(-)\)–S hydrogen bonding interaction with the optimized H···O distance of 1.88 Å is supplemented by an electrostatic interaction at a distance of 3.33 Å between the fum-carboxylate O atom and the \(\delta^+S\) atom of SO2 as well as (fum)C–S dispersion interactions. This site has the highest binding energy of \(-51.5\) kJ mol\(^{-1}\) of all found four higher-energy binding sites. The value is close to the experimental enthalpy of adsorption near zero coverage.
distorted. In the constrained structures, the parameters were fixed according to the crystal structure data. We also note variations in the optimized cell vector lengths and angles with respect to the crystal structure parameters. In Al-Fum, the b-vector lengthens by ca. 0.9 Å, while the respective a- and c-vectors shorten by 0.1 and 0.2 Å. The β-angle widens by ca. 5°.

For NH2-MIL-53(Al), we observe a lengthening in the b- and a-vectors of ca. 0.5 and 0.15 Å, respectively, and a shortening of 0.3 Å in the c-vector. The overall cell volume is mostly preserved in the optimized vacuum structure of Al-Fum. NH2-MIL-53(Al) has a ca. 3% larger cell size after full relaxation. Optimization of a single SO2 molecule within the structures partially results in further contraction along the c-axis in Al-Fum and additional lengthening along b in NH2-MIL-53(Al), indicating the breathing capability of both MOFs at low pressures (Figures 10 and 11). Interestingly, most of the computed high-energy binding modes (1–3) show this contraction along c and expansion along b.

The predominant noncovalent binding mode in sites 1–4 in Al-Fum (Figure 10a–e) can be traced to OH⋯δ−δ−OS hydrogen bonding interactions of SO2 with the μ-OH bridge and H⋯O distances from 1.98 to 2.82 Å. The binding site 1 (Figure 10a) with −51.1 kJ mol⁻¹ and with the shortest H⋯O distance is energetically close to binding sites 2 (−49.5 kJ mol⁻¹) and 3 (−48.6 kJ mol⁻¹). In the latter two sites, the small pores of Al-Fum allow the interaction of two μ-OH bridges from the opposite pore walls with the same SO2 molecule via OH⋯δ−δ−OS interactions, as well as (fum)C⋯δ+SO hydrogen bonds (Figure 10b,e). The experimental enthalpy of adsorption near zero coverage (ΔH_ads) in Al-Fum was −42 kJ mol⁻¹ (cf. Figure 7).

In the two lower-energy binding sites 4a and 4b of equal energy (−41.0 kJ mol⁻¹), again SO2 interacts through the framework by OH⋯δ−δ−OS and a (fum)CH⋯δ−δ−OS hydrogen bond in site 4a, while weaker H⋯O hydrogen bonding is observed in site 4b (Figure 10a,e). Additional (fum)CO⋯δ−δ−SO2 contacts as well as (fum)C⋯δ+SO dispersion interactions lead to the energy differentiation between the binding sites in Figure 10.

From the fully relaxed optimization of NH2-MIL-53(Al) with one SO2 molecule, we obtained at least four binding sites with binding energies ranging from −67.3 to −49.1 kJ mol⁻¹ (Figure 11a–d). Binding site 1 (Figure 11a) has the highest binding energy (−67.3 kJ mol⁻¹), and it is dominated by NH⋯δ−δ−OS hydrogen bonding and HN⋯δ−δ−OS electrostatic attractive interactions between −NH2 groups from two independent BDC-NH3 linkers. The value is again close to the experimental enthalpy of adsorption near zero coverage (ΔH_ads) in NH2-MIL-53(Al) of −67 kJ mol⁻¹ (cf. Figure 7). Binding site 2 (Figure 11b) has a slightly lower binding energy (−58.2 kJ mol⁻¹). Here, SO2 mainly binds to C6−π−δ from bdc-NH3 through C6−π−δ−δ−SO interactions with C6−π−δ−δ−SO distances between 2.99 and 3.19 Å. For binding site 3 (Figure 11c) with a binding energy of −55.1 kJ mol⁻¹, we note a NH⋯δ−δ−OS hydrogen bond, COO⋯δ−δ−SO electrostatic interactions, and weak CH⋯δ−δ−OS interactions as cooperating effects, trapping SO2 within the pores of NH2-MIL-53(Al). The shortest distances between SO2 and the ligands (NH⋯δ−δ−OS = 1.99 Å and CH⋯δ−δ−OS = 2.56 Å) in site 3 are between ligands on different Al atoms. Binding site 4 (Figure 11d) has the lowest binding energy (−49.1 kJ mol⁻¹); besides C6−π−δ−δ−SO and NH⋯δ−δ−OS interactions, an additional OH⋯δ−δ−SO hydrogen bond between μ-OH and SO2 contributes to the adsorption of SO2.
It should be noted that the free relaxation of Al-Fum and NH2-MIL-53(Al) cells for each binding site can give an additional contribution to the binding energy. Further, we simulated SO2 adsorption isotherms for Al-Fum in the pressure range of 0.01−1 bar at 293 K (Figure S58) using the GCMC program Cassandra (for computational details, see Section S7.3). The simulations were performed using either a fully relaxed geometry or the fixed cell parameters of the crystal structure data and by setting the Lennard-Jones parameter ε for aluminum either to 254.12 K (100%) or zero, allowing only electrostatic interactions with this atom type. The best agreement with our experimental data was achieved with the fixed geometry and ε(Al) = 0, which somewhat underestimated the SO2 adsorption capability or with the approach using the relaxed structure and ε(Al) = 100%, which overestimated the SO2 adsorption capability of Al-Fum.

The simulated isotherm data for Al-Fum was also used to model the pore filling in Al-Fum by a GCMC approach and is displayed in the form of single snapshots related to a defined pressure or as a movie, with a time-lapse over the complete pressure range (Figure S59 and Supporting Movies: SI-Al-Fum-2 kPa and SI-Al-Fum-0.05−100 kPa). Within the snapshots (e.g., at 2 and 3 kPa), it is observed that some pores are empty,
while nearby pores are already filled with multiple \( \text{SO}_2 \) molecules. This could be an indication of uneven filling of the pores, which might be caused by intermolecular dipole–dipole interactions of the \( \text{SO}_2 \) adsorptive process. It is recognized that the dipole moment of \( \text{SO}_2 \) plays an important role in the adsorption process with the pore filling occurring by (framework-)\( \text{O} \text{-} \text{S} \text{-} \text{O} \text{-} \text{S} \text{-} \text{O} \) and (framework-)\( \text{O} \text{-} \text{S} \text{-} \text{O} \text{-} \text{S} \text{-} \text{O} \) dipole–dipole interactions, forming \( \text{SO}_2 \) chains or clusters. However, this observation could also be assigned to “artifacts/ background noise” of the randomized Monte-Carlo simulations and thus needs further investigations.

**CONCLUSIONS**

Four Zr- and eight Al-MOFs, most of which are frequently investigated prototypical MOFs, were examined for their \( \text{SO}_2 \) adsorption capability to identify factors that influence the activity of \( \text{SO}_2 \) separations from \( \text{CO}_2 \) by MOFs. A strong correlation between the \( \text{SO}_2 \) uptake and BET-surface area and pore volume, at 1 bar and 293 K, was observed for all materials independent of their pore structure. Especially, MOFs featuring narrow pores with pore diameters between ~4 and 8 Å yielded high \( \text{SO}_2 \) affinities.

Also, amino groups at the linker tend to be advantageous for tuning \( \text{SO}_2 \) affinity. Among all tested MOFs, \( \text{NH}_2\text{-MIL-53(Al)} \), which combines both of the aforementioned properties, showed the highest \( \text{SO}_2 \) affinity and excellent low-pressure adsorption performance.

The chemical stability of MOFs vs acidic gases such as \( \text{SO}_2 \) over a prolonged time (10 h) and in the presence of moisture (for 5 h) presents a fundamental problem. Among the selected and proven water-stable Zr- and Al-MOFs, only Zr-Fum and DUT-67(Zr) could be called stable, while the other MOFs showed more or less loss of porosity, especially under the simultaneous presence of \( \text{SO}_2 \) and \( \text{H}_2\text{O} \). Interestingly, PXRD patterns were less indicative of framework degradation than losses in surface area (porosity). This suggests that degradation at the pore mouths leads to pore blocking, thereby leaving the inner framework of the MOF crystallites intact, albeit inaccessible.

Theoretical calculations on Zr-Fum, Al-Fum, and \( \text{NH}_2\text{-MIL-53(Al)} \) point also to metal-bridging \( \mu\text{-OH} \)- and \( \text{NH}_2 \)-groups in the SBU or at the linker as an important component of primary binding sites for \( \cdot\text{OH}^{\delta+}\text{-}\cdot\text{SO}_2 \) and \( \cdot\text{NH}_2^{\delta-}\text{-}\cdot\text{SO}_2 \text{OSO} \) hydrogen bonding interactions with binding energies of \(-50 \text{ kJ mol}^{-1}\) and above. At the same time, a low \( \text{CO}_2 \) affinity is required for trace \( \text{SO}_2 \) separation from flue gases. Calculated IAST selectivities for the highly \( \text{SO}_2 \)-affine MOFs, Zr-Fum, MOF-808, \( \text{NH}_2\text{-MIL-53(Al)} \), reached values above 40 for \( \text{SO}_2\text{/CO}_2 \) binary gas mixtures and low \( \text{SO}_2 \) mol fraction of 0.01 (1% or 10.000 ppm \( \text{SO}_2 \) ) at 1 bar.

In the end, this work not only gives a compilation of potential MOFs for possible use in adsorptive flue gas desulfurization processes but also offers guidelines to design new adsorbents for this important application.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c06003.

Synthesis of MOFs; additional MOF structure figures; powder X-ray diffractograms; gas sorption isotherms and measurement details; isotherm fitting and simulation parameters; details on DFT and GCMC calculations and simulations; and comparison of \( \text{SO}_2 \) sorption literature data (PDF)

**SL-AL-FUM-2 kPa (Movie) (MP4)**

**SL-AL-FUM-0.05—100 kPa (Movie) (MP4)**

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**Notes**

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**REFERENCES**


