

# Comparative Evaluation of Different MOF and Non-MOF Porous Materials for SO<sub>2</sub> Adsorption and Separation Showing the Importance of Small Pore Diameters for Low-Pressure Uptake

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Dedicated to Prof. Wolfgang Kaim on the occasion of his 70th birthday

The search for adsorbents for flue gas desulfurization processes is a current interest. For the first time, a comparative experimental study of SO<sub>2</sub> adsorption by porous materials including the prototypical metal–organic frameworks NH<sub>2</sub>-MIL-101(Cr), Basolite F300 (Fe-1,3,5-BTC), HKUST-1 (Cu-BTC), the zeolitic imidazolate frameworks (ZIF)-8, ZIF-67, the aluminosilicate Zeolite Y, the silicoaluminumphosphate (SAPO)-34, Silica gel 60, the covalent triazine framework (CTF)-1, and the active carbon Ketjenblack is carried out. Microporous materials with pore sizes in the range of 4–8 Å or with nitrogen heterocycles are found to be optimal for SO<sub>2</sub> uptake in the low-pressure range. The SO<sub>2</sub> uptake capacity at 1 bar correlates with the Brunauer-Emmett-Teller-surface area and pore volume rather independently of the surface microstructure. Zeolite Y and SAPO-34 are stable toward humid SO<sub>2</sub>. The materials Zeolite Y and CTF-1(600) show the most promising SO<sub>2</sub>/CO<sub>2</sub> selectivity results with an ideal adsorbed solution theory selectivity in the range of 265–149 and 63–43 with a mole fraction of 0.01–0.5 SO<sub>2</sub>, respectively, at 293 K and 1 bar.

containing CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>2</sub>.<sup>[1,2]</sup> For example, 43% of total SO<sub>2</sub> emissions (62.7 Mt in 2018) are related to coal combustion (27.0 Mt in 2018).<sup>[3]</sup> Emission of the toxic and acidic anhydride gas SO<sub>2</sub> is harmful to the biosphere and to human health both through air pollution and the formation of acid rain.<sup>[4,5]</sup>

The classic separation of SO<sub>2</sub> from flue gases is done by wet limestone-scrubbing or treatment by amine-based absorbents.<sup>[6]</sup> Flue gases generated by heavy oil- or coal combustion typically contain 500–3000 ppm of SO<sub>2</sub>, which can be reduced by up to 95% using these established methods.<sup>[7]</sup> Importantly, traces of SO<sub>2</sub> of <500 ppm remain in the flue gas and are emitted into the atmosphere. Also, this residual SO<sub>2</sub> inactivates CO<sub>2</sub> adsorbents or poisons selective NO<sub>x</sub>-oxidation catalysts.<sup>[8–10]</sup> A further decrease of the

SO<sub>2</sub> content in flue gases is therefore of high economic and environmental importance. Reversible SO<sub>2</sub> physisorption by porous materials is seen as a means to achieve a further SO<sub>2</sub> reduction in flue gases.

Currently, the SO<sub>2</sub> adsorption with metal–organic frameworks (MOFs) experiences high interest.<sup>[11–27]</sup> Metal–organic frameworks are typically microporous metal–ligand coordination networks with uniform porosity, low density, and high tunability through the organic linker, that is, the metal-bridging ligand.<sup>[28]</sup> MOFs are actively studied in the role of adsorbents (particularly N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, etc.) for prospective gas storage and gas separation<sup>[29–31]</sup> or the capture of toxic and polluting gases.<sup>[32–38]</sup> Yet, MOFs are often not of high chemical and hydrothermal stability.<sup>[39]</sup> An advantage of MOFs is clearly their designability, in particular their controllable pore size and modifiable pore surface is unmatched, yet, other porous materials may also feature good SO<sub>2</sub> uptake characteristics.


The main components of a typical flue gas mixture are N<sub>2</sub> or CO<sub>2</sub> with a minor part of SO<sub>2</sub> (500–3000 ppm).<sup>[7]</sup> Superior affinity to SO<sub>2</sub> over CO<sub>2</sub> and N<sub>2</sub>, which conditions high selectivity, is essential for reaching high efficiency of separation. A promising material should also possess a high SO<sub>2</sub> single-gas

## 1. Introduction

Over 85% of the global energy is still generated from the burning of fossil fuels leading to the emission of exhaust fumes,

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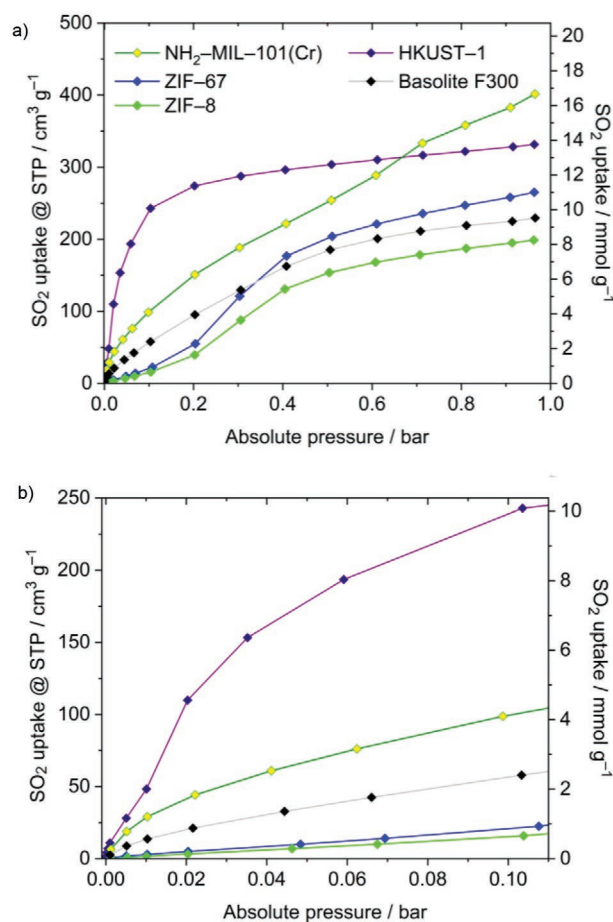
adsorption capacity in the low-pressure range without appreciable hysteresis. The overall potential of an SO<sub>2</sub> adsorbent depends also on stability and recyclability. SO<sub>2</sub> sorption materials should withstand corrosive conditions under dry and humid SO<sub>2</sub> exposure without a decrease in adsorption capability.<sup>[40]</sup> Further, the reversibility of the SO<sub>2</sub> adsorption at near room temperatures and energy-efficient recovery is crucial.<sup>[41]</sup> The prospective porous materials for reversible physisorption should be microporous ( $d_{\text{pore}} < 2$  nm), as adsorption should occur at low pressures to secure the removal of the relevant trace amounts of SO<sub>2</sub> from flue gases.<sup>[41]</sup>

In view of the current high interest on the physisorption of SO<sub>2</sub> with MOFs we are critically comparing here selected MOFs with other selected porous materials, namely the aluminosilicate Zeolite Y, the silicoaluminumphosphate (SAPO)-34, Silica gel 60, the covalent triazine framework (CTF)-1, and the active carbon Ketjenblack. The collected SO<sub>2</sub> adsorption data were used to verify existing simulation calculations<sup>[42–44]</sup> and assess the materials for their capabilities to remove low SO<sub>2</sub> concentrations from N<sub>2</sub>/CO<sub>2</sub>/SO<sub>2</sub> gas mixtures, with quantitative assessment of SO<sub>2</sub>/CO<sub>2</sub> selectivities using the ideal adsorbed solution theory (IAST) model. Furthermore, the relative stabilities toward dry and humid SO<sub>2</sub> gas were determined via a follow-up porosity and powder X-ray diffraction pattern analysis.

## 2. Results and Discussion

We selected the MOFs NH<sub>2</sub>-Matériaux de l'Institut Lavoisier (MIL)-101(Cr)<sup>[45,46]</sup>, Basolite F300<sup>[47,48]</sup> (also named Fe-1,3,5-benzenetricarboxylate (BTC)), Hong Kong University of Science and Technology (HKUST)-1<sup>[49,50]</sup> (also named Cu-BTC), the zeolitic imidazolate frameworks (ZIF)-8,<sup>[51,52]</sup> and ZIF-67<sup>[53,54]</sup> which can all be considered highly prototypical and which are intensely investigated toward application-oriented properties (see the Supporting Information for information on their structure). From the other porous material classes Zeolite Y,<sup>[55]</sup> the silicoaluminum phosphate SAPO-34,<sup>[56]</sup> Silica gel 60, the carbon–nitrogen framework CTF-1<sup>[57]</sup> (covalent triazine framework), and the active carbon Ketjenblack were investigated for SO<sub>2</sub> physisorption. Ketjenblack is a form of active carbon with high electroconductivity and a broad pore size distribution with a somewhat more ordered structure compared to other active carbons.<sup>[58,59]</sup> With this selection of materials we aim to cover a broad range of properties, e.g., pore size, functionality, open metal sites, etc. for comparative purposes (see Section S1, Supporting Information, for details). The MOFs NH<sub>2</sub>-MIL-101(Cr), HKUST-1, ZIF-8, and ZIF-67 were synthesized according to literature procedures and their identity was established by powder X-ray diffractometry (PXRD) and porosity analysis from nitrogen sorption isotherms (see the Supporting Information for details). The materials Basolite F300, Zeolite Y, SAPO-34, Silica gel 60, and Ketjenblack were purchased from commercial sources (see the Supporting Information for further information).

The individual SO<sub>2</sub> adsorption isotherms were measured at 293 K (Figures 1 and 2, for a combination, see Figure S22, Supporting Information) and the corresponding data together with the porosity characteristics from nitrogen sorption isotherms is given in Table 1. For clarity in the SO<sub>2</sub> sorption isotherm



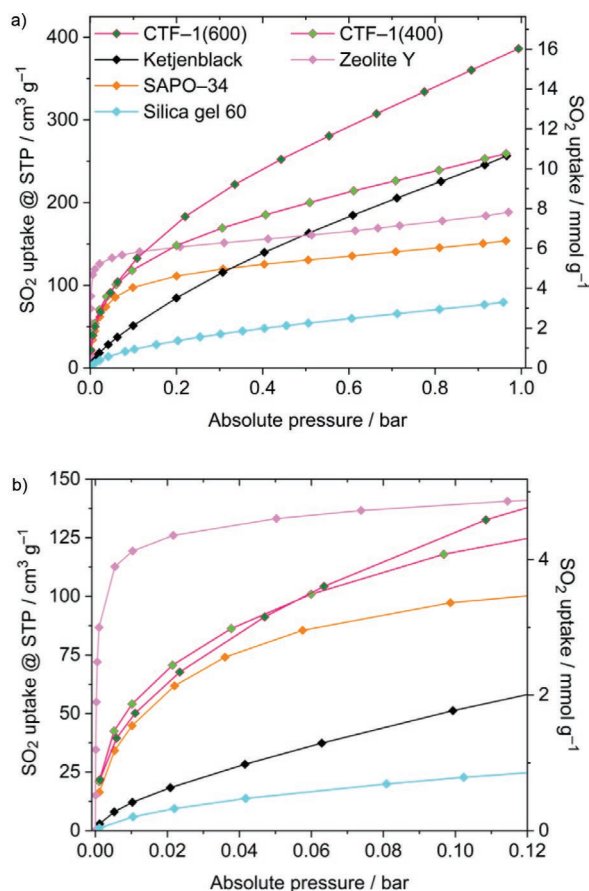
**Figure 1.** SO<sub>2</sub> adsorption isotherms (293 K) of the examined MOF materials: a) 0.001–1 bar and b) 0.001–0.11 bar. SO<sub>2</sub> desorption isotherms are omitted for clarity and are displayed in Figures S23–S29 in the Supporting Information.

diagrams we will present and discuss the MOF and the non-MOF materials separately.

### 2.1. SO<sub>2</sub> Adsorption by MOF Materials

The amino-functionalized MOF NH<sub>2</sub>-MIL-101(Cr) shows a moderate rise in SO<sub>2</sub> uptake in the pressure range from 0.001 to 0.1 bar with an SO<sub>2</sub> uptake of 4.1 mmol g<sup>-1</sup> at 0.1 bar. The SO<sub>2</sub> isotherm reflects a steady increase up to ambient pressures with a maximum SO<sub>2</sub> uptake of 16.7 mmol g<sup>-1</sup> at 1 bar without reaching a saturation stage. The adsorption isotherm is far from leveling off at 1 bar. This can be explained by relatively large micropores with a diameter of 15.4 and 19.9 Å for NH<sub>2</sub>-MIL-101(Cr) (vide infra).<sup>[70]</sup>

The amino functionalization of the MOFs was chosen as a possible factor, favoring adsorption of SO<sub>2</sub>, interpretable both as an interaction between basic and acidic species or as an interaction between polar species with enhanced dipole–dipole interactions.<sup>[19]</sup> Interestingly, however, NH<sub>2</sub>-MIL-101(Cr) shows no surface-specific enhancement of SO<sub>2</sub> uptake, i.e., the uptake per unit of the Brunauer-Emmett-Teller (BET) surface (see below),



**Figure 2.** SO<sub>2</sub> adsorption isotherms (293 K) of the examined non-MOF materials: a) 0.001–1 bar and b) 0.001–0.12 bar. SO<sub>2</sub> desorption isotherms are omitted for clarity and are displayed in Figures S23–S29 in the Supporting Information.

**Table 1.** SO<sub>2</sub> adsorption data and porosity characteristics at 293 K.

Material	Formula	SO <sub>2</sub> uptake [mmol g <sup>-1</sup> ] at			BET <sup>a)</sup> [m <sup>2</sup> g <sup>-1</sup> ]	Total pore vol. <sup>b)</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	Pore width <sup>c)</sup> [Å]	SO <sub>2</sub> /CO <sub>2</sub> selectivity <sup>d)</sup> at SO <sub>2</sub> /CO <sub>2</sub> molar ratio		
		0.01 bar	0.1 bar	1 bar				0.01	0.1	0.5
NH <sub>2</sub> -MIL-101(Cr)	[Cr <sub>3</sub> (O)(OH)(NH <sub>2</sub> -bdc) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1.2	4.1	16.7	2290	1.16	15.4, 19.9 <sup>[70]</sup>	34	30	30
Basolite F300; Fe(BTC)	n.a.	0.6	2.4	9.5	1070	0.49	18–22 <sup>[60]</sup>	n.d.	n.d.	n.d.
HKUST-1	[Cu <sub>3</sub> (1,3,5-btc) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]	2.0	10.1	13.8	1490	0.61	5, 11, 14 <sup>[61]</sup>	41	36	28
ZIF-8	Zn(2-Melm) <sub>2</sub>	0.1	0.7	8.2	1820	0.80	3.4, 11.4 <sup>[75]</sup>	n.d.	n.d.	n.d.
ZIF-67	Co(2-Melm) <sub>2</sub>	0.1	0.9	11.0	1980	0.69	3.4, 11.4 <sup>[75]</sup>	n.d.	n.d.	n.d.
Zeolite Y (NaY)	n.a.	5.0	5.8	7.7	930	0.33	7.4, 13.7 <sup>[62]</sup>	265	180	149
SAPO-34	n.a.	1.9	4.0	6.4	720	0.28	≈5 <sup>[63]</sup>	42	36	33
Silica gel 60	n.a.	0.2	0.9	3.3	540	0.75	≈10–100, av. 60 <sup>[64]</sup>	n.d.	n.d.	n.d.
CTF-1(400)	Ideally (C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>x</sub>	2.2	4.9	10.8	980	0.46	≈6–25 <sup>[65,66]</sup>	62	40	27
CTF-1(600)	Ideally (C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>x</sub>	2.1	5.5	16.0	2060	1.20	≈8–35 <sup>[66,67]</sup>	63	46	43
Ketjenblack	Ideally C	0.5	2.1	10.7	1410	1.24	≈20–80, av. 40 <sup>[68,69]</sup>	9	10	14

<sup>a)</sup>BET areas were calculated from five adsorption points of the N<sub>2</sub> isotherms within 0.05 < p/p<sub>0</sub> < 0.2. Values were rounded according to the estimated standard deviation of ±20 m<sup>2</sup> g<sup>-1</sup>. <sup>b)</sup>Total pore volumes were calculated from experimental N<sub>2</sub> sorption data at p/p<sub>0</sub> = 0.85–0.95, depending on the isotherm shape. For details see Section S2.3 in the Supporting Information; <sup>c)</sup>Pore widths as given in the literature; <sup>d)</sup>See Section S2.5 in the Supporting Information for the CO<sub>2</sub> sorption data. The MOFs Basolite F300, ZIF-8, ZIF-67, and Silica gel 60 did not show an appreciable SO<sub>2</sub> uptake at low pressure, hence the SO<sub>2</sub>/CO<sub>2</sub> selectivities were not determined (n.d.).

compared to other materials in this study. Ibarra et al. recently investigated SO<sub>2</sub> adsorption in the fluorinated MIL-101(Cr)4-F which shows a roughly similar isotherm shape to the isoreticular amino-functionalized frameworks but with slightly higher SO<sub>2</sub> adsorption capacity with uptakes of 4.6 and 18.4 mmol g<sup>-1</sup> at 0.1 and 1 bar, respectively, at 298 K and features exceptional stability against SO<sub>2</sub>.<sup>[71]</sup> This is in agreement with a smaller enthalpy of adsorption near zero coverage, ΔH<sup>0</sup><sub>ads</sub> = -36 kJ mol<sup>-1</sup> for NH<sub>2</sub>-MIL-101(Cr) (Figure S35, Supporting Information) than ΔH<sup>0</sup><sub>ads</sub> = -54 kJ mol<sup>-1</sup> for MIL-101(Cr)4-F.<sup>[71]</sup>

Basolite F300 shows somewhat lower SO<sub>2</sub> adsorption over the whole pressure range than NH<sub>2</sub>-MIL-101(Cr), reaching 9.5 mmol g<sup>-1</sup> at 1 bar.

The SO<sub>2</sub> isotherm of HKUST-1 features a single sharp increase in uptake to 10.1 mmol g<sup>-1</sup> at 0.1 bar, followed by a fast transition to near saturation with a maximum SO<sub>2</sub> uptake of 13.8 mmol g<sup>-1</sup> at 1 bar (a type-Ib isotherm by the International Union of Pure and Applied Chemistry (IUPAC) classification).<sup>[72]</sup> To the best of our knowledge HKUST-1 shows one of the highest SO<sub>2</sub> capacities with a type-I isotherm under ambient temperature and pressure ever reported. The remarkable uptake of HKUST-1 can be explained by the abundance of open metal sites (coordinatively unsaturated copper sites).<sup>[73]</sup> Our experimental results are in good agreement with simulation calculations for SO<sub>2</sub> in HKUST-1 carried out by Song et al. (sim./exp. at 298/293 K at 0.05 bar = ≈0.9/0.8 mmol g<sup>-1</sup> or 1 bar = ≈15/13.8 mmol g<sup>-1</sup>)<sup>[44]</sup> where absolute values deviate only slightly due to differences in accessible surface area. However, in subsequent stability tests, HKUST-1 showed no sustained stability (see below).

ZIF-8 and ZIF-67 both feature an unusual “S”-shaped (IUPAC type-V isotherm)<sup>[72]</sup> adsorption isotherm, with an initial stage at ≤ ≈0.1 bar where the adsorption is very low. The delayed SO<sub>2</sub> uptake for ZIF-8 was previously predicted by Sun et al. and Song et al. by simulation calculations and is in good agreement

with our experimental results.<sup>[43,44]</sup> The observation of “S”-isotherm shapes can be explained by the small pore entrance diameter of 3.4 Å<sup>[74,75]</sup> for both ZIF-8 and ZIF-67 and hence steric hindrance for the passage of SO<sub>2</sub> (kinetic diameter of 4.1 Å).<sup>[76]</sup>

The gate-opening effect occurring in both ZIFs, where the methyl groups of the ligand rotate due to the swinging of the imidazolate rings,<sup>[77]</sup> is the reason for the delayed rise in SO<sub>2</sub> adsorption occurs at ≈0.3 bar for both ZIF-8 and ZIF-67. The maximum SO<sub>2</sub> uptake reaches 8.2 and 11.0 mmol g<sup>-1</sup> at 1 bar, respectively.

## 2.2. SO<sub>2</sub> Adsorption by Non-MOF Zeolite Y, SAPO-34, Silica Gel 60, CTF-1, and Ketjenblack

From all examined materials the previously investigated Zeolite Y<sup>[78–80]</sup> shows the highest affinity toward SO<sub>2</sub> with exceptional uptake of 5.0 mmol g<sup>-1</sup> even at 0.01 bar (65% of the 1 bar capacity) with a fast transition into near saturation and maximum SO<sub>2</sub> uptake of 7.7 mmol g<sup>-1</sup> at 1 bar.

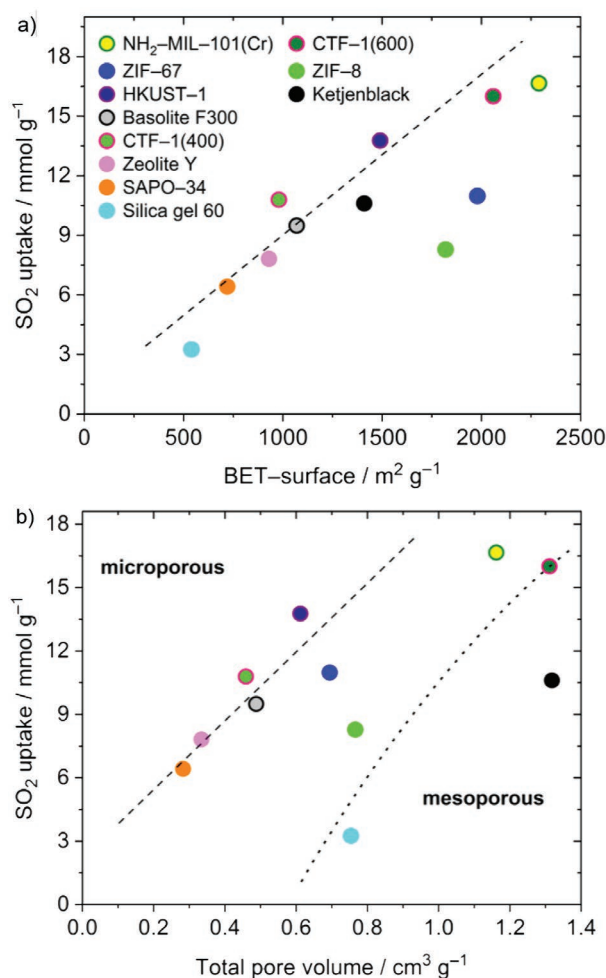
SAPO-34 shows a type-Ib SO<sub>2</sub> adsorption isotherm with an uptake of 4.0 mmol g<sup>-1</sup> at 0.1 bar, followed by a saturation stage with a maximum SO<sub>2</sub> uptake of 6.4 mmol g<sup>-1</sup> at 1 bar. The adsorption differences in Zeolite Y and SAPO-34 which have a broadly similar structure correlate rather well with the difference in surface area and pore volume. The high early uptake of both materials can be traced to their small pore sizes which favor multiple SO<sub>2</sub>-pore wall interactions (see below).

Silica gel 60 demonstrated a steady linear rise of SO<sub>2</sub> adsorption reaching an uptake of 3.3 mmol g<sup>-1</sup> at 1 bar, which is the lowest value in this comparative study. The effect could be explained by the combination of relatively low surface area and large pore sizes of the chiefly mesoporous Silica gel, which worsens the efficiency of the host-guest interactions. The saturation stage should be reached at pressures exceeding 1 bar.

The two covalent triazine frameworks (CTFs) CTF-1(400) and CTF-1(600) are synthesized at 400 and 600 °C, respectively. CTF-1(400) and CTF-1(600) show steep uptake steps with 4.9 and 5.5 mmol g<sup>-1</sup> adsorbed at 0.1 bar, followed by a nearly linear uptake reaching the values of 10.8 and 16.0 mmol g<sup>-1</sup> at 1 bar, respectively. Ketjenblack has a nearly linear uptake over the whole pressure range and arrives at an uptake of 10.7 mmol g<sup>-1</sup> at 1 bar. Neither of the three carbon materials reaches the saturation at 1 bar. Especially, the isotherms for CTF-1(600) and Ketjenblack still have a high positive slope and are far from leveling off at 1 bar. The superior affinity of the CTFs to SO<sub>2</sub> compared to Ketjenblack is likely due to the presence of smaller pore sizes in the former and more importantly due to stronger dipole-dipole interaction between the triazine and nitrile nitrogen atoms and SO<sub>2</sub>. The nitrogen atoms are primarily heteroaryl, but residual, unreacted terminal nitrile groups are also present.<sup>[81]</sup>

## 2.3. Structure-Adsorption Relationships

The surface area and the total accessible pore volume could be taken as the two primary factors governing the total SO<sub>2</sub> adsorption at 1 bar. The SO<sub>2</sub> uptake of all examined materials at 293 K



**Figure 3.** SO<sub>2</sub> uptake (1 bar, 293 K) versus a) BET-surface area and b) total accessible pore volume (both determined by N<sub>2</sub> adsorption at 77 K). The dashed trend lines are a guide to the eye. The dotted line in (b) separates the micro- and mesoporous materials.

and 1 bar is plotted against the BET-surface area and the pore volume in **Figure 3**. The examined materials differ significantly in terms of chemical composition and surface microstructure, nevertheless, the microporous materials without diffusion restriction show a reasonable correlation between SO<sub>2</sub> uptake and BET-surface area and total pore volume (**Figure 3**).

The two microporous ZIFs are noteworthy outliers in the uptake-surface area and pore volume correlation. This can be explained with the noted small pore window diameter of 3.4 Å<sup>[74,75]</sup> and steric hindrance for the passage of SO<sub>2</sub>. Above the threshold or gate-opening pressure of ≈0.3 bar, the SO<sub>2</sub> molecules could enter the pores. The two ZIFs are microporous materials with no mesopores. However, when probing the BET surface area, the smaller N<sub>2</sub> molecule with its kinetic diameter of 3.64 Å can more effectively cover the surface and fill the 11.4 Å diameter pore, than the larger SO<sub>2</sub> molecule with its kinetic diameter of 4.1 Å. Part of the pore surface and volume will remain inaccessible or empty with SO<sub>2</sub> due to steric hindrance from nearby adsorbates. A geometric estimate suggests that about 6 SO<sub>2</sub> molecules may fit into the 11.4 pore, while about 15 N<sub>2</sub> molecules can fill the same space. This effect of inaccessible surface is

especially pronounced in pores wider than the molecule length, but not wide enough for unrestrained surface coverage.

Also, the uptake of NH<sub>2</sub>-MIL-101(Cr), CTF-1(600), Ketjenblack, and Silica gel 60 is lower than expected from their surface area or pore volume which corresponds to the not reached saturation stage at 1 bar (see their above sorption isotherms). The total pore volume represents the limit for the maximum capacity. This is why the (partially) mesoporous materials are positioned below the linear trend line of the uptake versus surface area and pore volume dependence. The larger pores are not completely filled as the adsorption curve is far from saturation (in terms of an idealized Langmuir curve). The saturation uptake is only reached at pressures higher than 1 bar. The pore filling of such larger mesopores would have to occur by (framework-)O=S···O=S=O and (framework-)O=S=O···S=O dipole–dipole interactions, forming SO<sub>2</sub> chains or clusters. The dipole moment of SO<sub>2</sub> plays an important role in the adsorption process. In mesopores only part of the adsorbed SO<sub>2</sub> can interact with the surface. If in addition the surface of the mesoporous materials has only low affinity sites (e.g., Ketjenblack, Silica gel 60) then this contributes to the not reached saturation.

Most applications, including flue gas desulfurization or gas sensors, are restricted to gas mixtures with low partial pressures of SO<sub>2</sub>. The optimization of the material performance at low pressures ( $\leq 0.1$  bar) is therefore essential, whereas the total accessible pore volume should only be nonlimiting, i.e., only a certain threshold for the minimal uptake should be guaranteed. For the targeted low-pressure region, it is evident that there is no correlation between low-pressure SO<sub>2</sub> uptake and BET surface area (Figure S30, Supporting Information) and there is also no correlation of the SO<sub>2</sub> uptake to the micropore volume (Figure S31, Supporting Information).

For a high gas uptake at low pressure, that is a type-I isotherm, there must be a high affinity between the adsorbent and

the adsorbate. At low pressure, the adsorption affinity is synonymous with the uptake as long as the latter is not limited by surface area or accessible volume. The SO<sub>2</sub> adsorption isotherms of the materials were fitted with a Langmuir (LAI) or dual-site Langmuir (DSL) model yielding the affinity constants given in Table 2. The remarkably high initial SO<sub>2</sub> affinity constant of Zeolite Y (2739 bar<sup>-1</sup>) correlates with the higher initial uptake compared to SAPO-34 or CTF-1(400/600) with less steep uptake and thus yielding lower SO<sub>2</sub> affinity constants (95, 143, and 115 bar<sup>-1</sup>, respectively).

There is an optimum (or local optima) of pore size and pore shape for a given molecule. For example, one local optimum for a linear gas molecule with a length of  $L_{\text{ads}}$  is an adsorbent structure with opposite surfaces at a distance of  $L_{\text{ads}}$  between the Connolly surface, i.e., probe the accessible surface of the opposite sides.<sup>[72]</sup> This ensures optimal dispersive interactions with both ends of the molecule to the surface and this model is often used for computations.

The results of this study support the existence of an optimal pore size<sup>[18,26]</sup> for a high adsorption affinity of SO<sub>2</sub> at low pressures. The existence of such optimum is clearly visible by the maximum in the distribution of the surface-specific SO<sub>2</sub> uptake at 0.01 bar and 0.1 bar (293 K) against the pore limiting diameter (PLD), shown in Figure 4. As the absolute value of the uptake at low pressure depends on the surface area, it was normalized by division through the surface area, giving the surface-specific SO<sub>2</sub> uptake.

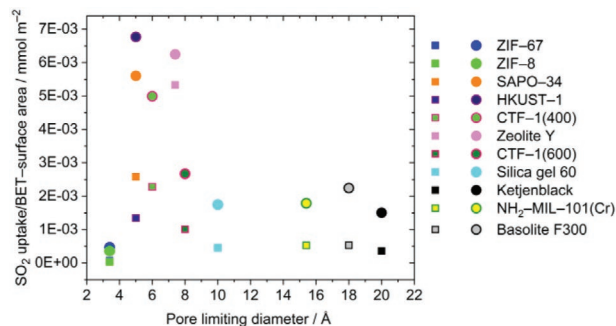
The PLD is the smallest diameter of a pore or window, present in a framework. The optimum pore width would be  $\approx 4\text{--}8$  Å, as found in HKUST-1, Zeolite Y, SAPO-34, and CTF-1(400). Porous materials with such pore widths exhibit a surface-specific SO<sub>2</sub> uptake larger than  $1 \times 10^{-3}$  or  $5 \times 10^{-3}$  mmol m<sup>-2</sup> at 0.01 or 0.1 bar, respectively. In contrast, materials with pores outside the above pore criteria exhibit a surface-specific SO<sub>2</sub> uptake smaller than  $0.5 \times 10^{-3}$  or  $2 \times 10^{-3}$  mmol m<sup>-2</sup> at 0.01 or 0.1 bar, respectively.

Grand-canonical Monte Carlo (GCMC) simulations for SO<sub>2</sub> sorption in MOFs, among them HKUST-1 and ZIF-8, also indicated that the amount of SO<sub>2</sub> adsorbed at 1 bar correlated neither well with the surface area nor with the total accessible pore volume. Instead, a good correlation of SO<sub>2</sub> uptake was found with the heat of adsorption in small pore ( $d_{\text{pore}} \geq 4$  Å) materials at 0.05 bar pressure.<sup>[44]</sup>

**Table 2.** Fitting parameters for SO<sub>2</sub>/CO<sub>2</sub> IAST-selectivities at 293 K.

Material <sup>a)</sup>	Gas	Model <sup>b)</sup>	Affinity const. [bar <sup>-1</sup> ]
NH <sub>2</sub> -MIL-101(Cr)	SO <sub>2</sub>	DSL	46.0
	CO <sub>2</sub>	DSL	9.6
HKUST-1	SO <sub>2</sub>	LAI	22.0
	CO <sub>2</sub>	LAI	0.4
SAPO-34	SO <sub>2</sub>	DSL	95.1
	CO <sub>2</sub>	DSL	5.5
Zeolite Y	SO <sub>2</sub>	DSL	2739
	CO <sub>2</sub>	DSL	9.3
CTF-1(400)	SO <sub>2</sub>	DSL	143.3
	CO <sub>2</sub>	DSL	6.1
CTF-1(600)	SO <sub>2</sub>	DSL	115.3
	CO <sub>2</sub>	DSL	10.5
Ketjenblack	SO <sub>2</sub>	LAI	0.9
	CO <sub>2</sub>	LAI	0.4

<sup>a)</sup>Basolite F300, ZIF-8, ZIF-67, and Silica gel 60 were not included in the IAST calculations for their low SO<sub>2</sub> uptakes at low pressures. The correlation coefficients for the isotherm fits were  $>0.996$ ; <sup>b)</sup>DSL = Dual-site Langmuir; LAI = Langmuir.



**Figure 4.** Surface specific SO<sub>2</sub> uptake (i.e., the total uptake divided/normalized by the BET-surface area) at 0.01 bar (squares) and 0.1 bar (circles) versus the pore limiting diameter. Note that for Silica Gel 60, CTF-1, and Ketjenblack only the smallest pore diameter is indicated and these materials have a broad pore size distribution (Table 1).

Furthermore, studies on  $\text{NH}_2\text{-MIL-125(Ti)}$  and  $[\text{Zn}_2(\text{L1})_2(\text{bpe})]$  indicate a positive effect of nitrogen functionalization to enhance the  $\text{SO}_2$  affinity at low pressures.<sup>[26,82]</sup> The effect could be operating here for CTF-1(400), CTF-1(600), and  $\text{NH}_2\text{-MIL-101(Cr)}$  and partially offset the (expected) lower uptake from the larger pore diameters.

In situ inelastic neutron scattering and density functional theory (DFT) calculations of  $\text{SO}_2$  at manchester framework material (MFM)-300(Al)<sup>[19]</sup> and in situ synchrotron PXRD studies on MFM-601(Zr)<sup>[83]</sup> had shown that stronger  $\text{SO}_2$  anchor points are also metal-OH groups as the hydrogen-bonding sites (metal-OH...O=S=O) for the first  $\text{SO}_2$  molecules. Here  $\text{NH}_2\text{-MIL-101(Cr)}$  and most likely Basolite F300 feature metal-OH anchor points. Also, the open metal sites in HKUST-1 are strong binding sites. However, in situ  $\text{SO}_2$  sorption synchrotron single-crystal X-ray diffraction experiments on the Cu(II) paddle-wheel MOF MFM-170 gave the open  $\text{Cu}^{2+}$  sites only as the secondary adsorption sites, where the  $\text{SO}_2$  molecule binds to in an end-on mode  $\text{Cu}\cdots\text{O}=\text{S}=\text{O}$  with 2.3(1) Å and an occupancy of only 0.67. Upon desorption the diffraction data under a dynamic vacuum at 298 K left the  $\text{Cu}^{2+}$ -bound  $\text{SO}_2$  with an occupancy of 0.09 which suggests that due to the Jahn-Teller effect the  $\text{Cu}-\text{O}=\text{S}=\text{O}$  bonding is weak so that it is almost entirely desorbed on the reduction of pressure.<sup>[21]</sup> On the other hand, ZIF-8 and ZIF-67 neither have metal-OH nor open metal sites, contributing to a low affinity, besides the low uptake due to the gate-opening effect (vide supra).

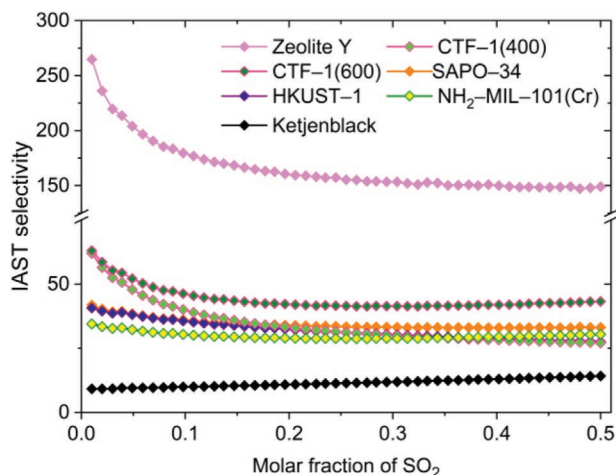
## 2.4. IAST Selectivity

$\text{CO}_2$  is the main competitor of  $\text{SO}_2$  regarding the binding to the adsorbent during the flue gas desulfurization. The  $\text{SO}_2/\text{CO}_2$  selectivity, which is crucial for the separation of gas mixtures, was assessed with the IAST model for some of the most promising materials using binary  $\text{SO}_2/\text{CO}_2$  mixtures. IAST-based estimations are adequate when the conditions of low relative pressures, similar polarity, as well as close molecular volumes of the components of the gas mixture, are fulfilled.<sup>[84]</sup>

The calculation of IAST-selectivities was performed by fitting the adsorption isotherm data points (Figures S23–S29 and Table S2, Supporting Information) using the “3P sim” software (parameters in Table S3, Supporting Information).<sup>[85]</sup>

The dependence of the calculated  $\text{SO}_2/\text{CO}_2$  IAST-selectivities on the mole fraction of  $\text{SO}_2$  (1 bar, 293 K) for all the examined materials are shown in Figure 5. Along with the order of Zeolite Y, CTF-1(600), CTF-1(400), SAPO-34, and HKUST-1 with  $\text{SO}_2/\text{CO}_2$  IAST-selectivities from 265, 63, 62, 42, and 41 these materials demonstrated the highest selectivities at 0.01 (10.000 ppm) molar fraction of  $\text{SO}_2$  (293 K and 1 bar). It is interesting that at a higher  $\text{SO}_2$  molar fraction of 0.5, the respective values become 149, 43, 27, 33, and 28 (293 K and 1 bar), i.e., the order changes somewhat. Overall, Zeolite Y shows the most promising result regarding the capture of  $\text{SO}_2$  from flue gas mixtures since it provides a high  $\text{SO}_2/\text{CO}_2$  selectivity and its type-I isotherm should allow a relatively small pressure interval for pressure swing adsorption processes.

Although, HKUST-1 shows decent  $\text{SO}_2/\text{CO}_2$  selectivity of 41 at a 0.01 molar fraction of  $\text{SO}_2$ , previously, Yaghi et al. and



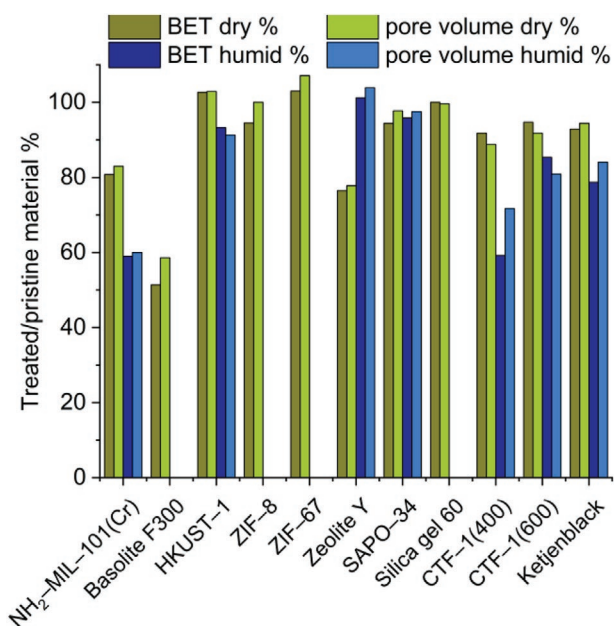
**Figure 5.**  $\text{SO}_2/\text{CO}_2$  IAST selectivity dependence on the molar fraction of  $\text{SO}_2$  in the range of 0.01–0.5 (293 K, 1 bar).

Jones et al. used HKUST-1 in breakthrough experiments in which the material showed no significant retention of  $\text{SO}_2$ .<sup>[32,86]</sup> Furthermore, a decreasing IAST-selectivity of HKUST-1 toward even lower  $\text{SO}_2$  partial pressures than 0.01 indicates that the material might not be able to separate trace amounts of  $\text{SO}_2$ . Noteworthy, HKUST-1 had the highest calculated selectivity for  $\text{NO}_x$  from GCMC simulations on a broad range of porous materials, including MOFs, ZIFs and zeolites with respect to a gas mixture of  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$ .<sup>[43]</sup>

Despite the high surface area of Ketjenblack the low affinity to  $\text{SO}_2$  results in its unremarkable  $\text{SO}_2/\text{CO}_2$  IAST-selectivity of 9 at a 0.01 molar fraction of  $\text{SO}_2$  (293 K and 1 bar).

## 2.5. Stability Test toward Dry and Moist $\text{SO}_2$

Stability tests of investigated materials were carried out with both dry and humid  $\text{SO}_2$  (the experimental methodology is given in the Supporting Information). From thermogravimetric analysis the porous materials show an initial water loss from their pores, but the frameworks are stable to 300 °C (Figures S32 and S33, Supporting Information). Humid  $\text{SO}_2$ , containing the moderately strong and quite corrosive sulfurous acid in equilibrium, reflects much better the real-world conditions in a potential sequestration application. The change of the BET-surface area and the total pore volume after  $\text{SO}_2$  exposure during the specified time was used as the primary stability indicator parameters (Figure 6 and Figures S11–S21, Supporting Information), while changes of the PXRD patterns were examined qualitatively (Figures S4–S10, Supporting Information). Note that the influence of humid  $\text{SO}_2$  exposure was mainly examined for materials that demonstrated both notable stability under dry  $\text{SO}_2$  exposure and remarkable  $\text{SO}_2$  affinity. While ZIF-8, ZIF-67, and Silica gel 60 were very stable toward dry  $\text{SO}_2$  (Figure 6), their affinity was low, hence neither of the three was subjected to humid  $\text{SO}_2$  anymore. It is worth mentioning that changes in the PXRD pattern were less prominent upon decomposition which is why a combination of diffraction and adsorption experiments is always recommended.



**Figure 6.** The relative (treated/pristine) BET surface area and total pore volume of investigated porous materials after dry and humid SO<sub>2</sub> exposure.

The dry SO<sub>2</sub> exposure during ≤10 h did not affect the majority of examined materials strongly (Figure 6). Most materials retained more than 90% of the BET-surface area and pore volume, in comparison to the untreated material. However, the amino-functionalized MOF NH<sub>2</sub>-MIL-101(Cr) as well as Basolite F300 demonstrated a major loss of porosity and were deemed SO<sub>2</sub>-unstable. We note that the parent MOF to NH<sub>2</sub>-MIL-101(Cr), namely MIL-101(Cr) is also not stable toward SO<sub>2</sub> which was explained by its comparatively hydrophilic nature.<sup>[71]</sup> We suggest that both NH<sub>2</sub>-MIL-101(Cr) and Basolite F300 are unstable because the SO<sub>2</sub> can interact with the metal-aqua and hydroxido ligand M-OH<sub>2</sub> and M-OH (Figure S1, Supporting Information), which are still present in both metal-cluster secondary building units (SBUs) after activation at 120 °C. Such an interaction can form sulfurous acid or hydrogen sulfite which may break the metal-carboxylate bonds with formation of metal-sulfite and the conjugated acid of the ligand. Mounfield et al. have performed in situ IR experiments on MIL-125 which confirmed the presence of bisulfite species and, in combination with computational simulations of formation energies of these adsorbed species, indicated that the degradation of the framework. The degradation likely proceeds through a reaction involving water, the dissociation of water or sulfurous or the combined reaction of sulfurous acid and water. Sulfurous acid, H<sub>2</sub>SO<sub>3</sub> can be formed from SO<sub>2</sub> with humidity inside the MOF.<sup>[87]</sup>

Under humid SO<sub>2</sub> exposure (35 ± 5 ppm) during 5 h SAPO-34 showed nearly no change in porosity and could be considered stable under both dry and humid conditions (Figure 6). CTF-1(600), Ketjenblack and surprisingly, HKUST-1 demonstrated moderate surface area loss under the humid-SO<sub>2</sub> exposure conditions. CTF-1(400) showed a more severe loss in surface area and pore volume toward humid SO<sub>2</sub>. When HKUST-1 was subjected to a humid SO<sub>2</sub> exposure time

of 8 and 24 h a drastic degradation of the framework structure became visible in subsequent PXRD and N<sub>2</sub> adsorption analysis (Figures S6 and S13, Supporting Information). Concerning, the initial higher stability of HKUST-1 in comparison to usually regarded more stable NH<sub>2</sub>-MIL-101(Cr) and Basolite F300 we refer again to the SBUs with their reactive metal-carboxylate bonds. The principle difference in the three SBUs is that the metal-aqua and -hydroxido ligands M-OH<sub>2</sub> and M-OH in NH<sub>2</sub>-MIL-101(Cr) and Basolite F300 are normally bound ligands where reaction with the SO<sub>2</sub> under formation of reactive sulfurous acid or hydrogen sulfite can occur (Figure S1, Supporting Information). Whereas in HKUST-1, the aqua ligand on d<sup>9</sup>-Cu(II) is subject to the Jahn–Teller distortion with an elongated Cu–O distance and weaker interaction (Figure S2, Supporting Information). This Cu-aqua ligand is easily removed upon activation. Further, sulfurous acid, which may still form, will also bind much weaker to Cu and thereby interact much slower with the Cu-carboxylate bonds.

Furthermore, SO<sub>2</sub> is also a strong reducing agent and may reduce the metal atoms in the MOFs to a lower valent state, such as Cr(II), Fe(II), and Cu(I). Upon reduction, the metal-carboxylate bonding can change more drastically, for example, high-spin d<sup>4</sup>-Cr(II) is also subject to Jahn–Teller distortion. In this regard, it is interesting to note that in activated HKUST-1 it was observed through the spectroscopic investigation of adsorbed CO<sub>2</sub>, CO, or NO that Cu(I) is present and coexists with Cu(II). Obviously, in HKUST the oxidation state of copper can be reduced to Cu(I) by redox treatments, using vacuum and/or reducing gases at different temperatures, albeit without noticeable framework degradation.<sup>[88–91]</sup> Hence, a higher “redox stability” could also be an explanation for the higher kinetic stability of HKUST-1 compared to the MIL frameworks.

A special case is Zeolite Y which exhibited better stability performance under humid exposure conditions than toward dry SO<sub>2</sub> (Figure 6). In the case of Zeolite Y, the accessibility and the location of the Na<sup>+</sup> counter cations to the anionic aluminosilicate framework contribute largely to the adsorption properties of this material.<sup>[92]</sup> Polar molecules, like water, can induce cation redistribution and thus change adsorption properties, e.g., selectivity and capacity, significantly.<sup>[93,94]</sup> So, it might be the case that preadsorbed water blocks or rather changes the accessibility for SO<sub>2</sub> in our experiment.

### 3. Conclusions

Five prototypical MOF materials were compared with six representatives of other classes of porous materials regarding their SO<sub>2</sub> adsorption capabilities. A strong correlation between the SO<sub>2</sub> uptake at 1 bar and 293 K and BET-surface area and pore volume was observed for all microporous materials, independently of their surface microstructure. The highest affinity constants toward SO<sub>2</sub> at low partial pressures (0.01–0.1 bar) were registered for materials featuring pores with diameters of ≈4–8 Å, and aromatic nitrogen atoms (e.g. CTFs).

The calculated IAST-selectivities for SO<sub>2</sub> over CO<sub>2</sub> were in the range of 9–265 (at 0.01–0.5 molar fraction of SO<sub>2</sub>), with the highest selectivity over the whole range given by Zeolite Y. Also, remarkable selectivities at low pressure were demonstrated by

CTF-1(400/600), which reflect the benefit of weakly basic acrylic nitrogens as more affine adsorption sites. When the stability toward humid SO<sub>2</sub> is further taken into consideration, this then leaves CTF-1(600), and SAPO-34 as the most promising materials for realistic use (i.e., humid conditions). The results of this work should raise the awareness for well-known porous material classes in the competition with currently advocated MOFs for SO<sub>2</sub> adsorption.

## 4. Experimental Section

**Materials:** The examined materials were synthesized according to published methods or obtained commercially (see Table S1, Supporting Information).

**Gas Adsorption:** BET characterization was performed on a Quantachrome Autosorb 6 automatic gas adsorption analyzer (further instrument). SO<sub>2</sub> and CO<sub>2</sub> isotherms were measured on a Quantachrome Autosorb iQ MP instrument. Before each experiment, the samples were activated according to the literature (but at least 3 h of degassing and a temperature of not less than 393 K) and a  $\approx 5 \times 10^{-3}$  mbar vacuum. All gases (He, N<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>) were of ultrahigh purity (99.999%). The standard temperature and pressure volumes at 293.15 K and 101.325 kPa are reported according to the recommendation of the National Institute of Standards and Technology. The N<sub>2</sub> adsorption experiments for the BET surface area and pore volume determination were performed within a pressure range of 0.005–1 bar at 77 K. The SO<sub>2</sub> sorption experiments were performed within a pressure range of 0.001–1 bar (0.96 ± 0.007 bar) and 293 K. A Dräger Pac 6000 electrochemical SO<sub>2</sub> sensor with a measuring range of 0.1–100 ppm was used for leakage testing and maintaining safe work conditions.

**Powder X-Ray Diffraction:** The PXRD measurements were performed on a Bruker D2 Phaser with a Cu-K<sub>α</sub> cathode source ( $\lambda = 1.54182$ ; 30 kV, 10 mA) at room temperature. The finely ground samples were measured in the range of  $5^\circ < 2\theta < 50^\circ$  using a low background silicon sample holder.

**Thermogravimetric Analysis (TGA):** TGA was performed on a Netzsch Thermo-Microbalance Apparatus TG 209 F3 Tarsus, at a heating rate of 10 K min<sup>-1</sup> under a nitrogen flow. Samples were not activated before the measurement.

**Stability Tests toward Dry and Moist SO<sub>2</sub>:** For the determination of the material stability under SO<sub>2</sub> exposure the change in BET surface area (N<sub>2</sub> sorption) and crystallinity (PXRD) were examined. Samples were activated as described above.

Stability tests toward dry SO<sub>2</sub> were carried out as the above SO<sub>2</sub> ad- and desorption isotherm measurement by exposing the sample between 8 h to less than 10 h under a variable pressure of 0.001–1 bar. Afterward the stability was assessed by the identity or changes in the PXRD and BET surface area and porosity.

Stability tests toward humid SO<sub>2</sub> were done in a self-constructed exposure chamber (Figure S2, Supporting Information), which contained a vessel of saturated sodium chloride solution (80 mL) to set a relative humidity (RH) of 75%. The chamber was filled with humid SO<sub>2</sub> by bubbling air through a solution of sodium hydrogen sulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> dissolved in water). The generated SO<sub>2</sub> concentration and the RH-value in the chamber were monitored by a Dräger Pac 6000 SO<sub>2</sub> sensor and a VWR TH300 hygrometer, respectively. The exposure was done at room temperature under an atmosphere containing 35 ± 5 ppm SO<sub>2</sub> and of 75 ± 6% RH humidity for 5 h. Experimental details and setup can be found in Section S2.1 in the Supporting Information.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

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active carbon, adsorption, metal–organic frameworks, MOFs, porous materials, sulfur dioxide, zeolites

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