

PAPER

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A Ni-based pyrazolate MOF (NiBDP) is studied for SO₂ adsorption under static conditions, demonstrating a high SO₂ uptake of 8.48 mmol g^{−1} at 298 K and 1 bar while maintaining a high chemical stability. The influence of Ni(II) coordinatively unsaturated metal sites and coordinated water on the SO₂ adsorption performance of this MOF is investigated by using a combination of experimental techniques, including FTIR and *in situ* DRIFTS measurements, along with Density Functional Theory calculations. The pore-filling of the SO₂ adsorbates within the material, at the molecular level, is further unravelled through grand Canonical Monte Carlo simulations employing a newly DFT-derived accurate set of force field parameters.

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Introduction

The standard families of porous materials, *e.g.*, activated carbons, zeolites, and mesoporous silica, have been extensively studied for the adsorption of small molecules within their porous cavities for diverse applications.^{1,2} More recently, metal-organic frameworks (MOFs), constructed by metal-containing nodes and organic linkers,³ which can propagate in one to three dimensions, have been shown to represent a milestone in the capture of greenhouse (CH₄ and CO₂)^{4–11} and toxic gases (NH₃, NO_x and SO₂).^{12,13} The diversity of metal ions and organic ligands that can be used for the construction of MOFs facilitates

their architecture design and, hence, the modulation of chemical features in the pore walls (*e.g.*, functionalization) and of pore dimension/shape to optimize the interactions with a given guest molecule.¹⁴ Therefore, a selection of MOFs has emerged as promising candidates in the field of material science for the adsorption of toxic and corrosive gases.¹⁵ Typically, SO₂ has gained a lot of interest since it is the main precursor of acid rain, and the hazardous effects of SO₂ on the environment and on human health are a huge concern. Thus, SO₂ capture by MOFs has been investigated since 2008, when Yaghi *et al.*,¹⁶ reported the SO₂ adsorption by several MOFs with diverse chemical and structural features. After two decades of worldwide efforts, certain chemical characteristics have been recognized to render MOF materials not only resistant to SO₂ exposure but also with attractive capture performance.^{17–19} These included the use of (i) high valent-metal ions, such as Zr⁴⁺, Al³⁺, In³⁺, and Sc³⁺ with carboxylate ligands; (ii) robust metal clusters with strong metal–ligand bonds, for example, the use of pyrazolate or imidazolate ligands and late transition M²⁺ ions; and (iii) the inclusion of coordinately unsaturated metal sites (CUS) or functional groups (X–H), capable of interacting with SO₂ by coordination bonds,²⁰ hydrogen bonds,²¹ and other supramolecular interactions.²²

Nickel(II)-based MOFs are *a priori* attractive sorbents owing to the good abundance of this metal and their usually high thermal and chemical stabilities. Moreover, from a chemical point of view, Ni-based compounds are known to exhibit interesting properties such as electrocatalytic capabilities,²³ magnetic properties,²⁴ energy storage,²⁵ and detection.²⁶ Although some M²⁺-based MOFs are considered unstable to SO₂

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surface area (SA), largest cavity diameter (LCD) and pore limiting diameter (PLD), were calculated by using Zeo++ software (see details for the calculations in the ESI†),⁴¹ and tabulated in Table S2.†

Force field parameterization

The consideration of generic force field for MOF frameworks combined with force field models for the guest molecules is known to dramatically fail to describe specific interactions between coordinative unsaturated MOFs with any guest molecules.^{42–46} Therefore, such MOF–CUS sites/guest molecule interactions require a specific FF parameterization based on first-principle quantum calculations. To do so, a 100% CUS containing model of the NiBDP MOF (*i.e.*, NiBDP-0H₂O) was first considered and an approaching path consisting of 10 different configurations associated to different SO₂–Ni CUS (NiBDP-0H₂O) separating distances were constructed while maintaining the same orientation as DFT-optimized minimum energy structure (Fig. S9†). Subsequently, single point energy calculations were performed to deduce the corresponding interaction energies for a SO₂ molecule within the NiBDP-0H₂O pore using the energy expression: $E_{\text{int}} = E_{\text{NiBDP-0H}_2\text{O}+\text{SO}_2} - (E_{\text{NiBDP-0H}_2\text{O}} + E_{\text{SO}_2})$, where, $E_{\text{NiBDP-0H}_2\text{O}+\text{SO}_2}$ corresponds to the single point energies of the SO₂ loaded NiBDP-0H₂O adsorption configurations along the interacting path, while $E_{\text{NiBDP-0H}_2\text{O}}$ and E_{SO_2} correspond to the energy associated to an empty NiBDP-0H₂O MOF and an isolated SO₂ molecule, respectively. The resulting interaction energy curve was then fitted to an analytical function combining van der Waals (vdW) and coulombic terms. Here, non-bonded interactions between SO₂ and NiBDP-0H₂O MOF atoms other than Ni(II) sites were modeled with standard Lennard-Jones (LJ) 12-6 potential while a Morse potential was employed to describe the interactions between SO₂ and Ni(II) atoms. The LJ parameters (ϵ and σ) for the MOF atoms were adopted from the universal force field (UFF),⁴⁷ whereas the SO₂ molecule was represented by the three-site LJ charged model reported by Ketko *et al.*,⁴⁸ (Tables S3–S5†). LJ cross-terms were then calculated using the Lorentz–Berthelot combination rules. The Ewald summation technique⁴⁹ was employed to compute the long-range coulombic contributions, in which, the atomic partial charges of the MOF are determined using the DDEC charge partitioning scheme as mentioned above, while the charges for SO₂ are obtained from the potential model of Ketko *et al.*⁴⁸ Finally, the Morse potential parameters, D , α , and r_0 associated with the Ni(II)–O(SO₂)– and Ni(II)–S(SO₂) specific interactions were determined using the General Utility Lattice Program (GULP)⁵⁰ by minimizing the energy differences with respect to the DFT counterpart. The corresponding fitting curve and the parameters are available in the ESI.†

Monte Carlo simulations

The SO₂ adsorption isotherms for all three NiBDP-*n*H₂O ($n = 0, 1, 2$) structures were calculated through the GCMC simulations implementing the force field discussed above using the Complex Adsorption and Diffusion Simulation Suite (CADSS) of the program.⁴² Nonetheless, for the NiBDP-2H₂O structure, the SO₂ adsorption isotherm was computed by using generic UFF parameters for all framework atoms, as the system does not

contains any CUS sites. We employed a simulation box comprising eight-unit cells ($2 \times 2 \times 2$) of the MOFs. The atomic positions of the MOFs' skeletons were held fixed during the adsorption, and Monte Carlo trial moves for the guest molecules. The host–guest nonbonded interactions were computed in real space using a cutoff of 12.0 Å. The long-range electrostatic interactions were calculated using the Ewald summation technique⁴⁹ with an accuracy of 1×10^{-6} . For each pressure point, 1×10^7 and 2×10^7 Monte Carlo steps including insertion/deletion, translation and rotational moves, were considered for equilibration and production, respectively. The Peng–Robinson equation of state was used to determine the gas-phase fugacity for SO₂ molecules.⁵¹ The overall adsorption isotherms were obtained by running GCMC simulations for different fugacities ranging from 10^{-4} to 1 bar. Additionally, the enthalpy of SO₂ adsorption at infinite dilution was computed employing Widom's test particle insertion method.⁵²

Results and discussion

Characterization of NiBDP

NiBDP MOF was synthesized according to the reported procedure.³¹ This structure crystallizes in the face cubic centered (fcc) topology with the $Fm\bar{3}m$ space group. Each Ni(II) ion is bonded to three N atoms from different organic linkers, and three of the six μ_4 -O observed in the octanuclear cluster (Fig. 1a). It is important to note that two of the six oxygen atoms belong to coordinated water molecules rather than hydroxo ligands.⁵³ The structure contains two types of cages: an octahedral cage (diameter of ~ 16 Å) connecting to eight tetrahedral cages (diameter of ~ 9 Å) accessible *via* triangular windows (diameter of ~ 6 Å), (Fig. 1b, c and S1†). In the octahedral cage, the OH groups point toward the centre of the pore, which can favor interactions with SO₂ in addition to the Ni(II) sites, as it was demonstrated for other materials, such as the MFM-300 family.⁵⁴ The crystalline structure was confirmed by PXRD (Fig. S2†). Based on N₂ sorption measurements at 77 K (Fig. S3†), the activated NiBDP shows a BET surface area of 1220 m² g^{−1}, which is lower than the previously reported (1730 m² g^{−1}).⁵⁵ The corresponding theoretically calculated surface areas of NiBDP-0H₂O and NiBDP-2H₂O are 2650 m² g^{−1} and 2480 m² g^{−1}, respectively, suggesting that the CUS sites of the investigated sample are not fully evacuated. In addition, elemental analysis (EA) of NiBDP [Ni₈(OH)₄(H₂O)₂(BDP)₆](H₂O)₂(DMF)₁₀] was conducted. Anal. calc. for NiBDP (2589.90 g mol^{−1}) C, 47.3; H, 5.06; N, 18.4; Ni, 18.1, found C, 46.7; H, 5.10; N, 18.2; Ni, 18.8. Nickel content was determined on the basis of TGA (Fig. S4†). Also, electronic spectra (Fig. S5†) characterization is indicative of the presence of the characteristic d–d transition bands of Ni(II) in a poorly distorted Oh environment (${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, 10 350 cm^{−1}; ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, 15 870 cm^{−1}; ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, 25 800 cm^{−1}).

SO₂ sorption in NiBDP

Previously, the SO₂ capture in NiBDP was reported using breakthrough experiments for an N₂/SO₂ mixture. However,



under these conditions, a relatively low SO_2 concentration ($P_{\text{SO}_2} = 0.025$ bar) was considered. NiBDP showed a total uptake of 2.02 mmol g^{-1} at 303 K. The SO_2 affinity was attributed to the Lewis acid–base interactions with crystal defects.³⁰ However, equilibrium adsorption–desorption isotherms are more appropriate to gain deep insights into the adsorption capacity, adsorption mechanism and to understand the adsorption behavior of certain gases within a porous material.⁵⁶ Thus, the SO_2 adsorption–desorption isotherms were investigated for NiBDP. The corresponding SO_2 sorption isotherm is shown in Fig. 2. A steep profile is observed in the adsorption isotherm from 0 to 0.025 bar. At this stage, SO_2 adsorption reaches a value of 1.85 mmol g^{-1} and remains almost constant up to 0.45 bar (1.89 mmol g^{-1}). This SO_2 uptake is similar to that reported so far for other MOFs like MFM-133 (1.2 mmol g^{-1}),⁵⁷ MFM-422 (1.8 mmol g^{-1}),⁵⁷ SIFSIX-3-Zn (1.89 mmol g^{-1}),⁵⁸ and ELM-12 (1.95 mmol g^{-1})⁵⁹ at 0.1 bar implying that NiBDP can be used as an alternative SO_2 adsorbent at low gas pressures. Interestingly, a sharp jump in the SO_2 adsorption capacity from 1.89 mmol g^{-1} up to 7.22 mmol g^{-1} is observed at 0.45 bar, which ultimately reaches a total SO_2 uptake of 8.48 mmol g^{-1} at 1 bar. The latter value is comparable to a variety of MOF materials such as UiO-66-Cu,⁵⁷ MFM-300(In)⁶⁰ and MIL-53(Al)-TDC⁶¹ with a reported SO_2 uptake of 8.2 mmol g^{-1} , 8.28 mmol g^{-1} , and 8.9 mmol g^{-1} , respectively, under similar working conditions (1 bar and 298 K). Considering the experimental BET surface area of NiBDP ($1220 \text{ m}^2 \text{ g}^{-1}$), the SO_2 uptake of 8.48 mmol g^{-1} aligns well with other microporous MOFs with similar surface area, for instance, UiO-66, possessing the same fcu topology and a BET surface area of $1221 \text{ m}^2 \text{ g}^{-1}$, can adsorb 8.6 mmol g^{-1} of SO_2 at 298 K and 1 bar.⁵⁷

Interestingly, the adsorption isotherm profile is unusual for a well-defined microporous MOF. In the low-pressure region, a rapid adsorption profile is defined, which can be related to a high interaction between the Ni^{2+} CUS sites and the SO_2

molecule, which can be postulated as a possible main adsorption site for NiBDP and gives rise to adsorbate seeding in the pore structure.⁶¹ Then, a subsequent almost horizontal plateau is observed, which can be associated with the presence of weaker interaction sites such as water molecules and hydroxide groups coordinated to the Ni^{2+} sites. Later, the sudden step at 0.45 bar followed by a linear adsorption (SO_2 saturation up to 1 bar) should be related to an adsorbate clustering, giving rise to pore filling. The observed seeding and clustering adsorption behavior can be related to the water adsorption mechanism unraveled for the MOF-303 system.⁶²

Finally, the retention of NiBDP crystallinity after SO_2 adsorption was corroborated by PXRD analysis (Fig. S2†), demonstrating that the inclusion of polyazolate-containing ligands and borderline soft acid Ni^{2+} in MOFs improves their structural stability against corrosive gases.⁶³

Furthermore, the isosteric enthalpy of adsorption (ΔH) for SO_2 adsorption was calculated at low coverage using the virial method (Fig. S6†).⁶⁴ The calculated value at low SO_2 loading (<0.03 bar) is $-41.2 \text{ kJ mol}^{-1}$, which is in good agreement with the value reported in earlier ($-40.1 \text{ kJ mol}^{-1}$).³⁰ This relatively high value can be associated with moderately strong SO_2 interaction with NiBDP. Typically, a MOF material with CUS sites usually shows a high ΔH value ($-80/-90 \text{ kJ mol}^{-1}$) due to the strong coordination between the metal and the SO_2 molecule.²⁶ The lower value obtained here can be related to a decrease in the availability of Ni^{2+} CUS sites due to the presence of coordinated water.

FTIR and DRIFTS analysis in NiBDP

FTIR experiments were carried out on a NiBDP sample before and after exposure to SO_2 gas and moisture traces to confirm the stability (Fig. S7†). The FTIR spectra of NiBDP show the characteristic bands for a pyrazolate MOF material. The bands related to C=O and C=C are associated with the peaks at 1649 and 1574 cm^{-1} , respectively.⁶⁵ The bands at 1410 and 1385 cm^{-1} are related to C=N. The bands at 1240 and 510 cm^{-1} are assigned to N–N bonds in the organic linker and the coordination bonds between Ni and N, respectively.⁶⁶ Also, after SO_2 adsorption show different bands from the region $1800-450 \text{ cm}^{-1}$ (Fig. 3a). Two principal SO_2 bands at 1153 cm^{-1} and 1303 cm^{-1} are observed, that are related to asymmetric and symmetric stretching modes of SO_2 molecules within the pores. This type of interaction agrees with SO_2 physisorption on $\text{Ni}(\text{BDC})(\text{TED})_{0.5}$ with bands at 1144 and 1326 cm^{-1} .⁶⁷ Finally, the formation of hydrolyzed species of SO_2 (i.e., SO_3^{2-} or HSO_3^{2-}) due to the presence of water is discarded due to the lack of characteristic IR bands for these ions.

In addition, *in situ* DRIFTS measurements were conducted using CO as a probe molecule. This technique is a powerful tool to characterise acid/base sites for different porous materials, including MOFs.⁶⁸ Even though the chemical nature of CO is different to SO_2 , this study is useful to gain insight into the possible adsorption sites for the guest molecules, as previously reported⁶⁹ in particular to make the distinction between the interactions with Ni^{2+} CUS sites or the coordinated water

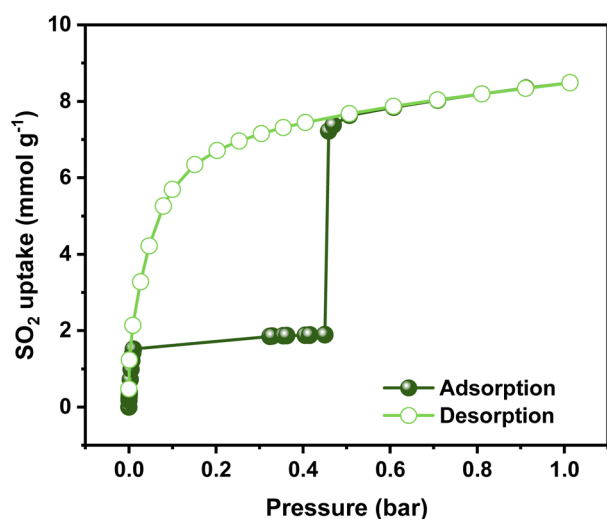


Fig. 2 Experimental SO_2 adsorption–desorption isotherm of an activated NiBDP sample (filled green circles = adsorption; open green circles = desorption) at 298 K up to 1 bar.

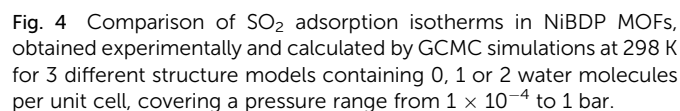




The IR spectra of the activated sample are shown in Fig. S8.† When the sample was activated at 70 °C, broadband was observed between 3450 and 3200 cm⁻¹. On the other hand, when the sample was activated at 190 °C, this band partially

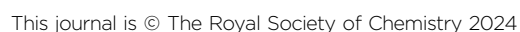
To analyze the difference in CO adsorption between the two activation methods, a subtraction of the spectra before and after the admittance of CO was carried out. Fig. 3c shows the subtracted spectra. It is evident that a peak appears at 2109 cm^{-1} when the sample is activated at $70\text{ }^{\circ}\text{C}$. This peak was already assigned to the adsorption of CO over metallic Ni.⁷⁰ Therefore, the DRIFT analysis confirms that both Ni^{2+} CUS sites and coordinated water can interact with the guest molecules in activated NiBDP sample.

To further gain insights into the effect of Ni^{2+} CUS sites and coordinated water molecules in the SO_2 adsorption, the adsorption of SO_2 in NiBDP with and without evacuated Ni(II) CUS sites were systematically studied through GCMC simulations to fully understand the resulting adsorption behavior. As a starting point, we computed the SO_2 single component adsorption isotherm for NiBDP- $2\text{H}_2\text{O}$ MOF at 298 K, covering a pressure range from 1×10^{-4} to 1 bar, and by using the generic UFF potential parameters as the system does not contain CUS sites. As illustrated in Fig. 4, our GCMC simulations result in an SO_2 uptake of 15.2 mmol g^{-1} for this NiBDP- $2\text{H}_2\text{O}$ structure at 1 bar, which exceeds the experimentally determined maximum uptake of 8.48 mmol g^{-1} . This deviation



Consequently, GCMC simulations performed utilizing our newly DFT-derived $\text{SO}_2/\text{Ni(II)}$ force fields effectively reproduce the

Furthermore, the enthalpy of adsorption calculated at very low coverage SO_2 adsorption is found to be $-113.0 \text{ kJ mol}^{-1}$ in excellent agreement with the DFT calculated binding energy. These attributes provide a clear indication of achieving an accurate adsorption isotherm at low pressure using this newly derived force field. Indeed, as shown in Fig. 4, the GCMC calculations effectively reproduce the shape of the experimental SO_2 adsorption isotherm at low pressure ($1 \times 10^{-4} \text{ bar}$). NiBDP-



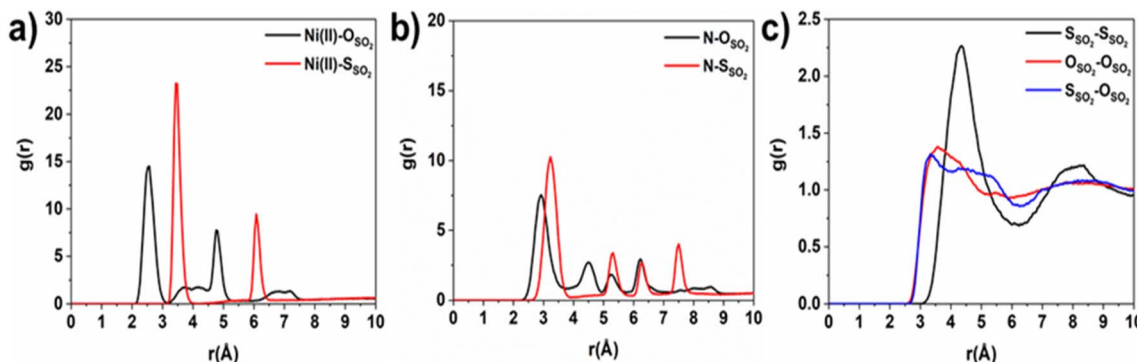


Fig. 6 Intermolecular radial pair distribution functions of NiBDP-0H₂O MOF atoms and adsorbed SO₂ molecules were calculated at $P = 0.10$ bar (a and b), and guest SO₂-SO₂ (c) was calculated at $P = 0.50$ bar.

2H₂O shows a distinct SO₂ adsorption isotherm profile at low pressure associated with a simulated adsorption enthalpy of -45 kJ mol^{-1} , more in line with the experimental data that suggests that the activated sample still contains a large concentration of coordinated water. As expected, NiBDP-1H₂O is in-between.

A deeper analysis of these simulated isotherms at very low-pressure regions (1×10^{-4} to 0.1 bar) unravels the SO₂ adsorption mechanism in all NiBDP- n H₂O ($n = 0, 1, 2$) systems. However, depending on the availability of CUS sites in NiBDP frameworks, the amount of SO₂ uptake varies, with NiBDP-2H₂O, NiBDP-1H₂O and NiBDP-0H₂O showing 0.00 mmol g^{-1} , 0.55 mmol g^{-1} and 1.12 mmol g^{-1} at 1×10^{-4} bar, respectively. This highlights that the presence of CUS sites in the NiBDP framework enhances SO₂ uptake at a very low-pressure domain. Nevertheless, for all three NiBDP MOFs, our GCMC-predicted SO₂ isotherms exceed the experimental results above 0.2 bar, which may be attributed to differences in the experimentally and theoretically calculated BET surface area (see above).

Conclusions

In summary, a Ni(II)-based pyrazolate MOF, NiBDP, has been investigated for SO₂ adsorption under static conditions. This material exhibits exceptional chemical stability and a maximum SO₂ adsorption capacity of 8.48 mmol g^{-1} at 298 K and 1 bar and an unusual step isotherm. Molecular simulations reveal that the SO₂ uptake of this material strongly depends on the concentration of Ni CUS sites and the presence of coordinated water molecules with stepwise seeding and clustering of adsorbate molecules. FTIR and *in situ* DRIFTS experiments corroborated the presence of coordinated water molecules and the availability of Ni(II) CUS sites in the structure simultaneously. A microscopic picture of the SO₂ adsorption mechanism has thus been gained in line with the unusual adsorption isotherm profile exhibited by this material. Thereby, the study highlights the relevance of robust Ni-pyrazolate MOF materials for high SO₂ stability.

Conflicts of interest

There are no conflicts to declare.

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