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Dedicated to Professor Stefan Kaskel

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ABSTRACT

Biomethane (CH_4) combustion, as a renewable fuel, is an excellent alternative to decrease the CO_2 emissions released into the atmosphere. However, this combustion requires catalysts which are normally poising by the presence of SO_2 gas. Then, an auxiliary material capable of selective capturing the contaminant SO_2 is necessary. In this work, the SO_2 gas adsorption performance of a high stable Al(III) MOF known as DUT-4 was studied. In addition to the high SO_2 uptake, in dry and wet conditions, and a high SO_2 adsorption cyclability, we have explored for the first time a promising purification of CH_4 in presence of SO_2, taking into account the high affinity for SO_2, even at a low concentration of SO_2 (a molar gas composition of 1:99 SO_2:CH_4).

1. INTRODUCTION

Global warming is a huge threat to human health and to the environment. This problem not only affects the ecosystem by creating stronger and more frequent storms, floods, heatwaves, and droughts but also can deteriorate heavily human health.[1] Global warming is created by a set of gases known as greenhouse gases: nitrous oxide (NO_x), fluorinated gases, carbon dioxide (CO_2) among others.[2] The indiscriminate and excessive use of fossil fuels *e.g.*, coal, natural gas, and oil, is the main responsible for the increase of such gases especially the CO_2 emission and its release to the atmosphere. For example, in 2018, the Environmental Protection Agency (EPA) reported a CO_2 consumption of close to 7000 million metric tons.[3]

Biogas is a highly desirable green energy source and an appealing alternative to reduce CO_2 emissions from the burning of fossil fuels.[4] This renewable fuel is commonly constituted by methane (50-75%), carbon dioxide (25-50%), and other gases in small amounts such as N_2, NH_3, H_2, volatile organic compounds, and H_2S (from ppm to 1%).[5] Although, the composition of biogas lacks SO_2 this air pollutant can be generated by the oxidation of H_2S in the biogas combustion process.

The optimization of engines in heavy-duty vehicles relies on efficient internal combustion by the implementation of a less polluting source of fuel such as biomethane that can lead to a 27% reduction of CO_2 emissions.[6] Biomethane is the main quality fuel from the biogas separation process by removing the CO_2 excess. According to Wang and co-workers, a methane oxidation catalyst (MOC) that uses d^7 metal centers (*i.e.*, Ni(II), Pd(II), and Pt(II)), is an excellent alternative to improve the fuel combustion performance of heavy duty vehicles.[7] Unfortunately, these catalysts are very sensitive to nucleophilic attacks resulting in a deactivated state (catalyst poisoning). Therefore, due to the high temperatures that are necessary for the operation of MOCs

and their reactivation and considering the small amounts of H_2S mixed in the bio-methane flow, H_2S is completely oxidized to SO_2 that can immediately react with the catalyst forming MSO_x species (catalyst poisoning). For example, Kinnunen and Auvinen demonstrated that MOCs show low tolerance to SO_2, impeding its reuse and fundamentally "killing" the catalyst over consecutive re-activations.[8] Thus, it is fundamental for the MOCs to implement a cooperative operation of an auxiliary adsorbent material that shows high selectivity of SO_2/CH_4 and structural stability at high temperatures to avoid catalyst poisoning.

A relatively new class of highly crystalline-porous materials known as metal-organic frameworks (MOFs) has gained distinct attention for the capture of SO_2, with the prime condition to be chemically stable towards this corrosive gas.[9] The capture of this harmful gas (SO_2) in MOFs has been demonstrated to be a complex task due to the formation of a strong and occasionally irreversible bond (*e.g.*, metal−sulfur bond) which can disrupt other coordination bonds between the metal centers and ligands, endorsing a structural collapse.[10] However, selected chemically-stable MOFs to SO_2 have been presented by Schröder,[11] Navarro,[12] Eddaoudi,[13] Janiak,[14] Ibarra[15] and others. In particular, the hydroxo-functionalized MFM-300(M) (MFM = Manchester Framework Material, M = Al^{3+}, In^{3+}, and Sc^{3+})[16] family has been demonstrated to be chemically stable towards SO_2 with the particularity of using, for their construction, trivalent metal centers which allow the formation of stronger M-O bonds with carboxylate ligands compared to divalent ions.[17] Therefore, herein we deliberately explored the SO_2 adsorption properties of another well-known trivalent metal-centered-based MOF, namely the DUT-4.[18] This microporous Al(III) MOF is constructed with Al(III)-oxygen octahedra linked to a 2,6-naphthalene dicarboxylate (ndc) ligand. DUT-4 shows an orthorhombic crystalline structure with a channel-like porosity of 8 Å associated with a moderate BET area (S_{BET} =1308 $m^2 \cdot g^{-1}$). In

addition, DUT-4 possesses high thermal stability (up to 500 °C), making it suitable for high-temperature applications. Accordingly, this material has been successfully tested for sulfoxidation reactions,[19] productions of solvent-free cyclic carbonates,[20] CO_2 adsorptions,[21] siloxane adsorption for biogas purification,[22,23] and hydrogen storage.[24] We revealed that DUT-4 shows promising SO_2 capture performance with adsorption capacity at 1 bar among the best MOFs with similar pore volume reported so far combined with a good cyclability, and easy adsorption reversibility. In addition, the high thermal stability and the robust structure of DUT-4 postulate it as a potential candidate for applicability in CH_4 purification even in the presence of traces of SO_2, due to the high affinity for SO_2 molecules. Thus, DUT-4 could also be considered as an interesting candidate as a matrix support for the MOC process. Molecular simulations were performed to shed light on the microscopic SO_2 adsorption mechanism and further predicted DUT-4 to be highly selective for the binary SO_2/CH_4 mixture that makes this MOF highly attractive for CH_4 cleaning.
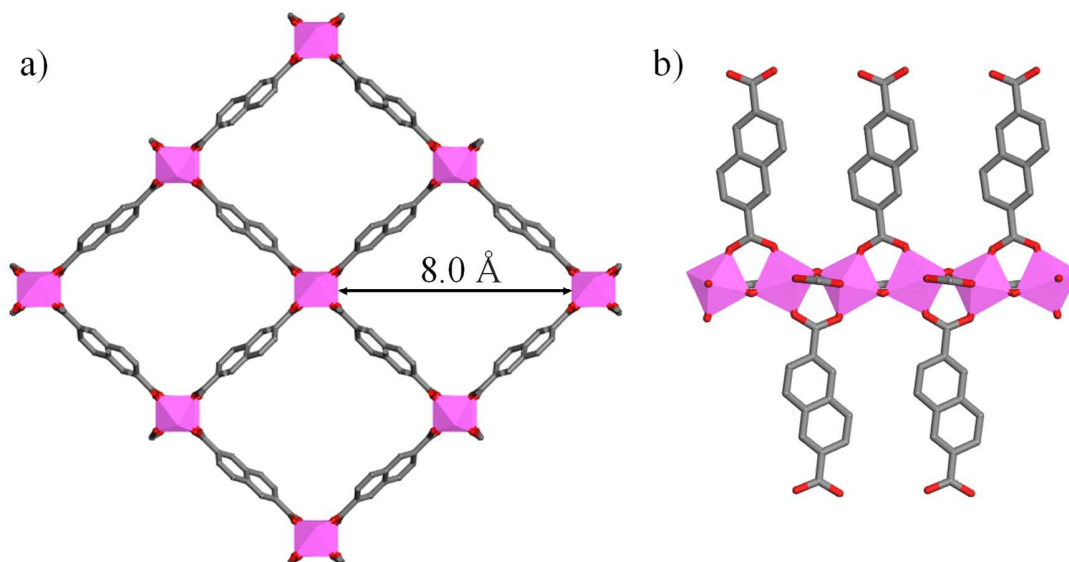
Figure 1. Structure of DUT-4 (a) along the channel *c*-axis and (b) metal cluster and linker arrangement along the *b*-axis. Atoms label: pink: $AlO_4(\mu\text{-}OH)_2$ octahedra, grey: carbon and red: oxygen.

2. EXPERIMENTAL SECTION

2.2 Synthesis and characterization

The synthesis of DUT-4 was carried out as reported by Kaskel and co-workers.[18] First, a solution of 2,6-naphthalene dicarboxylic acid, also known as H_2NDC linker (Sigma Aldrich, 95 %, 0.26 g) in *N,N*-dimethylformamide (Sigma Aldrich, DMF, 30 mL) was mixed with nonahydrate aluminum nitrate (Sigma Aldrich, 98 %, 0.52 g) in a Teflon Liner. Then, the liner was placed into an autoclave at 120 ℃ for 24 h. After that, the autoclave was opened at room temperature, and the product was washed with 20 mL of DMF and centrifuged for 2.5 min at 10 000 rpm three times. Finally, the product was dried for 4 h at 120 ℃ in an oven.

All reagents and solvents were used as received from commercial suppliers without further purification. FT-IR spectra were obtained in the range of 4000-500 cm^{-1} on a Bruker Tensor 27 spectrometer with a Golden Gate Single Reflection diamond ATR cell. Solid-state ^{27}Al MAS NMR spectra were recorded at room temperature on a Bruker Avance III HD NMR spectrometer (20 kHz, 0.27 μs length pulse, 1s delay, 2000 scans). Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu $K\alpha_1$ (λ= 1.5406 Å). Thermal gravimetric analysis (TGA) was performed under N_2 at a scan rate of 2 °C/min using a TA Instruments Q500HR analyzer. N_2 adsorption was carried out in a conventional volumetric technique using Micromeritics ASAP 2020. The surface area was calculated using the BET method based on adsorption data in the partial pressure (p/p_0) range of 0.01 to 0.04.

2.2 SO$_2$ and CH$_4$ Adsorption Experiments.

SO$_2$ isotherms were recorded at 298 K and up to 1 bar with the aid of a Dynamic Gravimetric Gas/Vapor Sorption Analyzer, DVS Vacuum (Surface Measurements Systems Ltd.) SO$_2$ was purchased from INFRA. CH$_4$ adsorption isotherms were recorded on a Micromeritics ASAP2020 at 298 K up and to 1 bar. CH$_4$ was purchased from PRAXAIR.

2.3 Computational studies

Initial atomic coordinates for DUT-4 were taken from a previously reported study[18]. The Lennard Jones (LJ) parameters for the organic and inorganic parts of DUT-4 were taken from DREIDING[25] force field and the UFF[26] force field respectively. The partial atomic charges for each framework atom of DUT-4 were extracted from periodic Density Functional Theory (DFT) calculations using the ESP[27] method as implemented in Dmol$_3$ and the PBE[28] functional and the DNP[29] basis set. The SO$_2$ molecule was represented by the microscopic model reported by Ketko *et al.*[30] This corresponds to a rigid model where both three charged LJ sites are centered in the atomic positions, with a S-O bond of 1.432 Å and a O-S-O bond angle of 119.3 °. The CH$_4$ was represented by the uncharged United atom UA TraPPE model.[31] The DUT-4/SO$_2$ interactions were described using a 12-6 LJ potential and a coulombic contribution while the DUT-4/CH$_4$ interactions were described only with a 12-6 LJ potential. Using a general approach adopted in previous studies,[32] the H atom from the μ-OH group and the Al atoms interact with SO$_2$ only via electrostatic interactions. LJ crossed parameters between the MOF material and the guest molecules were calculated with the Lorentz-Berthelot mixing rules. A cut off distance of 12 Å was used for the LJ contributions, while the long-range electrostatic interactions were handled with the Ewald summation technique.[33]

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of DUT-4

The PXRD pattern of the MOF sample is the same than the one assigned to DUT-4, according to the characteristic peaks at 6.95º, 13.91º, and 21.04º (Figure S1)[18] The textural properties of DUT-4 were obtained from N_2 adsorption-desorption isotherms (Figure S2). The estimated BET area and pore volumes are 1348 $m^2 \cdot g^{-1}$ and 1.71 $cm^3 \cdot g^{-1}$, consistent with previously reported data for this solid.[18,24] The coordination of the organic linker to the inorganic cluster was evidenced in the FT-IR spectra by the absorption band peak corresponding to the stretching vibration of the carbonyl groups (1690-1667 cm^{-1}, Figure S3). Asymmetric stretching vibrations of the carboxylate groups were recorded at 1614-1598 cm^{-1}. The bands related to the stretching vibrations of the aluminum atom with oxygen atoms were observed between 586-561 cm^{-1}. The ^{27}Al NMR spectra revealed a strong resonating signal at -7.0 ppm, which corresponds to six-fold coordinated aluminum sites (Figure S4).[34] To sum up, all reported characterization studies confirmed the successful synthesis of DUT-4.

3.2 SO₂ adsorption-desorption measurements

Prior to SO_2 assessments, a DUT-4 sample was degassed by an acetone-exchange (10 days) and heated up at 190° C under vacuum for 12 h to ensure the removal of the solvent synthesis (DMF) from the channels. Figure 2 depicts the SO_2 adsorption-desorption isotherms at 298 K and 1 bar for the activated MOF. The adsorption branch is a standard type-I characteristic of microporous solids. From 0 to 0.05 bar (Figure S5), the SO_2 adsorption capacity shows a discrete increment close to 2.4 $mmol \cdot g^{-1}$. The SO_2 adsorption suddenly reaches 9.8 $mmol \cdot g^{-1}$ in the 0.05-0.2 bar

pressure range. Finally, at 1 bar, the maximum adsorption capacity is 13.6 mmol·g^{-1}. As expected, the maximum capacity of DUT-4 is substantially higher than its rigid and flexible analog MIL-53(Al)-TDC and MIL-53(Al)-BDC (8.9 and 10.8 mmol·g^{-1}, respectively),[15] and even it is higher to other representatives MOFs with higher surface areas (above 1550 m^2·g^{-1}) such as MIL-601 (12.3 mmol·g^{-1}),[35] MFM-202 (10.2 mmol·g^{-1}),[36] among others (See Table S1). Further, the adsorption and desorption branches are very similar, the absence of a hysteresis suggesting a total reversible adsorption process. PXRD and FT-IR analysis show that DUT-4 remains unaltered after the SO$_2$ adsorption-desorption cycle (Figure S6 and S7). Furthermore, Figure 2 inset shows that the SO$_2$ adsorption isotherm for DUT-4 is well reproduced by the Grand Canonical Monte Carlo (GCMC) simulations (see ESI for computational details). This observation emphasizes that the optimal SO$_2$ adsorption performance is achieved for the activated DUT-4.
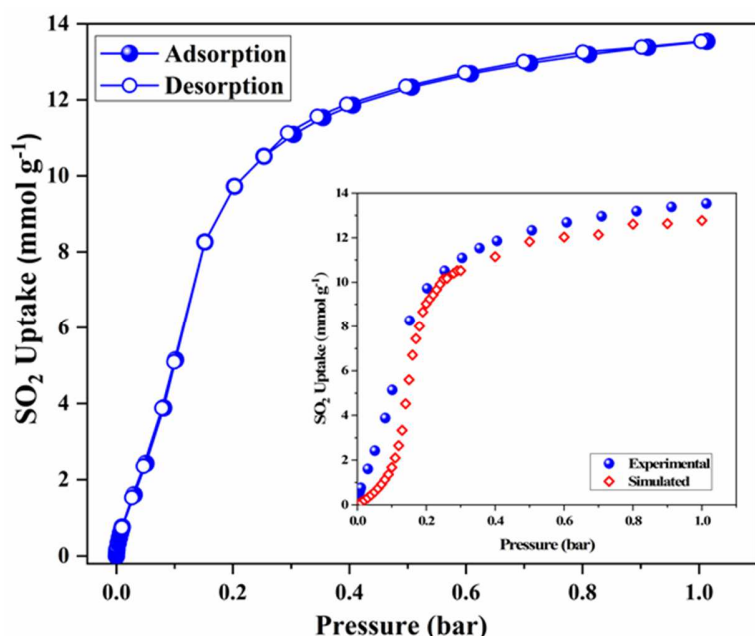
Figure 2. SO$_2$ capture at 298 K for DUT-4. Solid circles represent adsorption, and open circles show desorption. The inset shows the comparison between the experimental (filled blue circles) and GCMC simulated (open red diamond) SO$_2$ adsorption isotherms.

The simulated SO$_2$ adsorption enthalpy of -31.3 kJ·mol^{-1} at low coverage is lower than the values we previously calculated for the MIL-53(Al)-TDC and MIL-53(Al)-BDC (-41.0 kJ·mol^{-1} and -50.6 kJ·mol^{-1} respectively)[15] analogs. This trend is consistent with a less steep adsorption profile at low pressure for DUT-4 as compared to the other two solids.[15] Further analysis revealed that at low loading, SO$_2$ can interact with both the μ-OH group and the organic linker of DUT-4, as illustrated by the GCMC snapshot reported in Figure 3a. This preferential geometry is associated with mean O(SO$_2$)-H(org) and O(SO$_2$)-H(μ-OH) distances of 2.9 Å and 2.7 Å respectively as reported in the Radial Distribution Function (RDF) plots for the corresponding pairs (Figure S10).
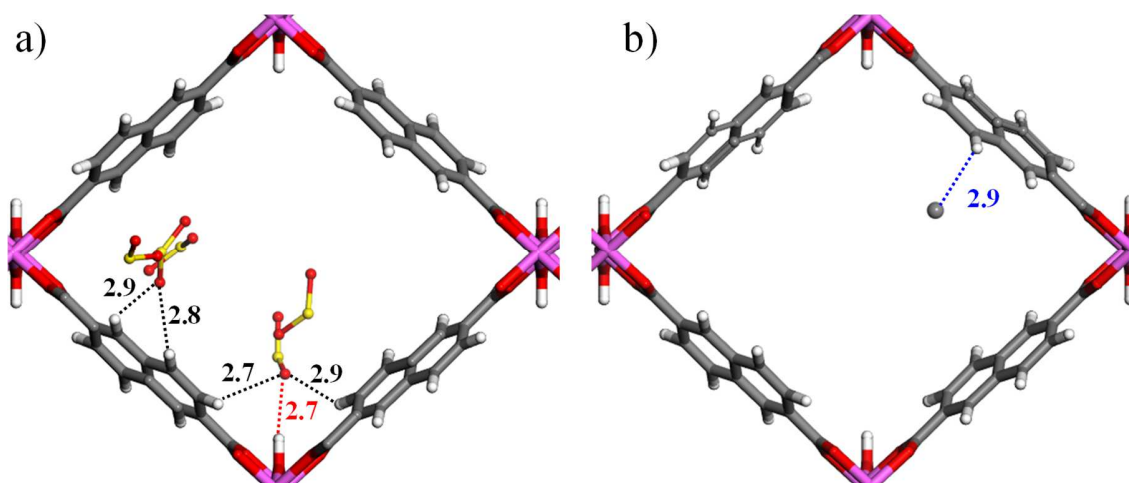

Figure 3. Illustration of the GCMC simulated (a) SO$_2$ and (b) CH$_4$ arrangements in the pores of DUT-4 in the case of the single component adsorption at very low loading. Color code: (Al,

pink; O, red; S, yellow; C, grey; H, white). The distances are reported in Å, O_{SO2}–$H_{\mu\text{-OH}}$ (red), O_{SO2}–H_{org} (black) and C_{CH4}–H_{org} (blue).

The structural stability of the DUT-4 was evaluated under more realistic conditions (60% relative humidity, See SI).[10] An activated sample (*vide supra*) was exposed to wet SO_2 in a homemade system for 24 h. The resulting PXRD pattern confirmed the retention of crystallinity after exposure to this condition, and FT-IR did not detect any local structural change for the MOF material (Figure S6 and S7). Further, to evaluate the SO_2 adsorption-desorption continuing performance, fifty SO_2 adsorption-desorption cycles were recorded from 0 to 1 bar under dry conditions (Figure 4). Remarkably after 50 cycles, the maximum SO_2 adsorption capacity decreases only by 5%.
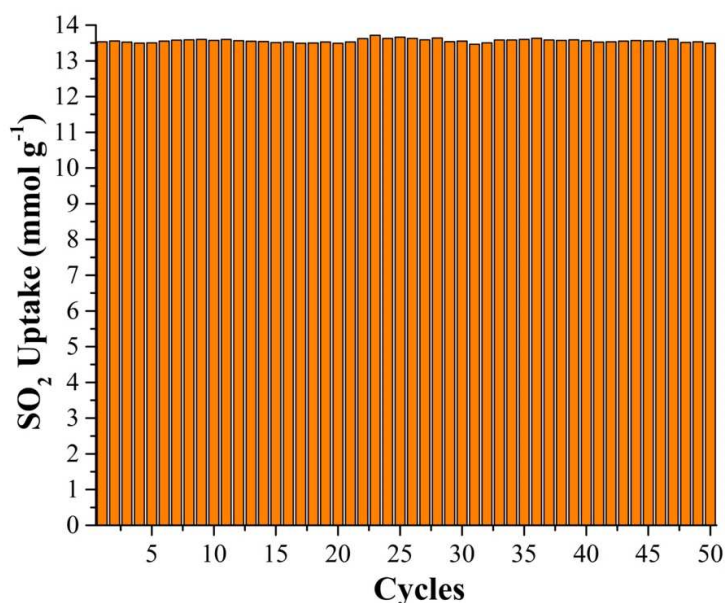

Figure 4. Adsorption–desorption cycles for SO_2 in dry conditions in DUT-4 at 1 bar and 298 K.

As a further stage, GCMC simulations were employed to explore the adsorption of CH_4 first as a single component in DUT-4. Figure 5a shows that the simulated adsorbed amount of CH_4 is

much lower compared to SO_2 in good agreement with the experimental adsorption isotherm also collected for CH_4. The calculated adsorption enthalpy of -12.4 kJ·mol^{-1} is also lower in line with only weak van der Waals CH_4/DUT-4 interactions with the adsorbate being in the vicinity of the organic linker (see Figure 3b) with a mean C(CH_4)-H(org) distance of 2.9 Å as defined by corresponding RDF plot (Figure S10). This single component adsorption behavior encouraged us to computationally assess the separation performance of DUT-4 for a model binary SO_2/CH_4 molar 1:99 mixture composition. The resulting simulated co-adsorption isotherms reported in Figure 5b confirmed a much higher affinity of DUT-4 for SO_2 vs CH_4, the amount adsorbed of SO_2 being similar to that obtained as a single component (Figure 5a). Remarkably, these calculations predict an almost full exclusion of CH_4 over SO_2 that makes this material highly attractive for cleaning CH_4.
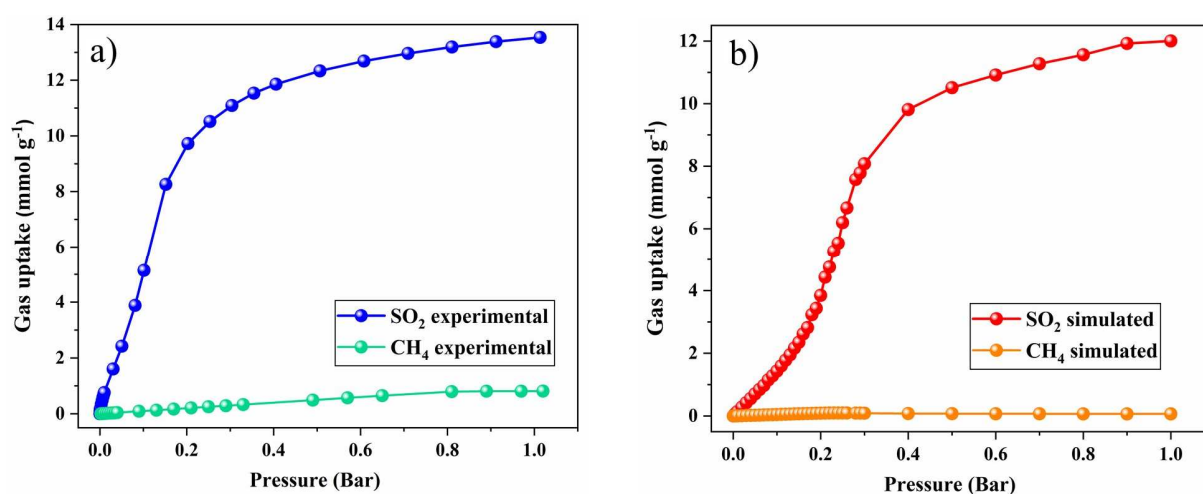

Figure 5. (a) Experimental-simulated single component adsorption isotherms for SO_2 and CH_4 at 298 K and up to 1 bar. (b). Simulated co-adsorption SO_2/CH_4 isotherms with a molar gas composition of 1:99 respectively. In a. filled blue and green circles = SO_2 and CH_4 experimental

single isotherms, respectively and filled red and orange circles = SO_2 and CH_4 simulated isotherms with a molar gas composition of 1:99 respectively.

To support this prediction, we further qualitatively assess the separation ability of DUT-4 using a simple model that consists of evaluating the α^{37} factor as a ratio of the gas uptake of SO_2 and CH_4 as single components (see SI). We found that the α factor is 67.2 and 49.5 at 0.05 and 0.2 bar respectively. Indeed, this experimental finding confirms that DUT-4 can be considered as a promising adsorbent for the selective capture of SO_2 from methane thus offering an opportunity to circumvent the poisoning issue of the methane oxidation catalyst mentioned above.

4. CONCLUSIONS

In summary, DUT-4 exhibits a high SO_2 adsorption capacity at 298 K and 1 bar, very good chemical stability towards dry SO_2, and a high SO_2 cyclability (up to 50 cycles). Furthermore, this Al(III)-MOF was shown to exhibit a remarkable affinity for SO_2 over CH_4 in the whole pressure range (1 bar). This performance was corroborated by computational studies showing that the μ-OH is the preferential SO_2 adsorption site at low pressure. These findings postulate DUT-4 as a promising adsorbent to clean CH_4.

ASSOCIATED CONTENT

Supporting Information. PXRD data, FTIR data, adsorption data, molecular simulation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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