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A fine-tuned fluorinated MOF addresses the needs for trace CO₂ removal and air capture using physisorption.

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ABSTRACT: The development of functional solid-state materials for carbon capture at low carbon dioxide (CO₂) concentrations, namely from confined spaces (<0.5 %) and in particular from air (400 ppm), is of prime importance with respect to energy and environment sustainability. Herein, we report the deliberate construction of a hydrolytically stable fluorinated metal-organic framework (MOF), **NbOFFIVE-1-Ni**, with the appropriate pore system (size, shape and functionality), ideal for the effective and energy-efficient traces carbon dioxide removal. Markedly, the CO₂-selective **NbOFFIVE-1-Ni** exhibits the highest CO₂ gravimetric and volumetric uptake (ca. 1.3 mmol/g and 51.4 cm³(STP).cm⁻³) for a physical adsorbent at 400 ppm CO₂ and 298 K. Practically, the **NbOFFIVE-1-Ni** offers the complete CO₂ desorption at 328 K under vacuum with an associated moderate energy input of 54 kJ/mol, typical for the full CO₂ desorption in conventional physical adsorbents but considerably lower than chemical sorbents. Noticeably, the contracted square-like channels, affording the close proximity of the fluorine centers, permitted the enhancement of the CO₂-framework interactions and subsequently the attainment of an unprecedented CO₂-selectivity at very low CO₂ concentrations. The precise localization of the adsorbed CO₂ at the vicinity of the periodically aligned fluorine centers, promoting the selective adsorption of CO₂, is evidenced by the single-crystal X-ray diffraction study on the **NbOFFIVE-1-Ni** hosting CO₂ molecules. Cyclic CO₂/N₂ mixed-gas column breakthrough experiments under dry and humid conditions corroborate the excellent CO₂-selectivity under practical carbon capture conditions. Pertinently, the notable hydrolytic stability positions the **NbOFFIVE-1-Ni** as the new benchmark adsorbent for direct air capture and CO₂ removal from confined spaces.

INTRODUCTION

Mitigating the amount of the CO₂ released in the atmosphere, directly correlated to the global warming, remains an ongoing challenge that requires a concerted worldwide effort from academia, industry and governments alike. Inopportunistically, the worldwide energy needs have doubled the fossil fuel consumption in the last two decades,¹⁻¹¹ as a result of the eminent economic growth and the enhanced quality of living in emerging countries, and thus provoking the manifest and amplified global carbon dioxide emission. The foreseen deployment of a relatively cleaner alternative energy sources, e.g. solar, renewable and nuclear, to meet the increasing global energy demand, while lessening or eliminating the CO₂ emission as a result of deserting the dominant use of the fossil fuel, is still universally debated and implausible in the near future.¹⁻¹¹ In view of that and while preparing for the looked-for fossil-fuel free transition, it is evidently necessary to develop new technologies and materials for the effective and energy-efficient carbon dioxide (CO₂) capture in a wide range of concentrations. Explicitly, point-source carbon capture and storage (CCS) can be regarded as a plausible solution sanctioning the sustainable use of fossil fuels in power, steel and cement production plants, while direct air capture (DAC) can address and remediate the CO₂ emissions from mobile-sources such as

automobiles and airplanes.¹⁻¹¹ Markedly, the DAC offers a great prospective to remotely capture the emitted CO₂ at a different distant location and time.

It is to note that the CO₂ capture from air using the chemical adsorption technology has been deployed, for over seven decades, to maintain a safe level of CO₂ in confined spaces such as space shuttles and submarines, where access to fresh air is limited.^{12,13} Nevertheless, the CO₂ concentrations and the associated CO₂ quantities to the DAC (400 ppm CO₂, worldwide average of 54 kg/person/day) and to the point-source CCS (7-15% CO₂, worldwide average of 38 kg/person/day) entail a relatively larger scale footprint and/or an excessive energy penalty than the requisites for the CO₂ capture in confined spaces (1-5 % CO₂ and 1 kg/person/day).¹⁻¹¹ Perceptibly, the cost associated to the CO₂ capture in confined spaces is not a disturbing concern, as the compulsory objective is the effective removal of CO₂ and the subsequent procurement of the indispensable clean air.

Noticeably, the low CO₂ concentration in air (400 ppm) and the compulsory low CO₂ level in confined spaces (< 0.5 %) position chemical adsorbents, such as aqueous alkylamine solutions and lithium hydroxide (LiOH) (80-120 kJ/mol), as the conventional benchmark materials, with a high CO₂-selectivity even in the presence of water vapor, for the carbon

capture in diluted CO₂ concentrations.⁸ Nevertheless, large-scale widespread of the chemically driven separation approach is hampered by the prohibitive high-energy requirement for the CO₂ desorption/regeneration process. Markedly, there is a need to develop a new generation of highly CO₂-selective physical adsorbent materials with a moderate CO₂ heat of adsorption, i.e. below 60 kJ/mol.^{3,14-17} Consequently, such a looked-for adsorbent will pave the way to an affordable, effective and energy-efficient recovery of CO₂ and renders the DAC competitive and self-sustainable. Considerately, the aerospace industry recognized the advantages of the physisorption-based separation and recently shifted their efforts to the utilization of recyclable physical adsorbents, such as the zeolite 5A (Ca²⁺) and the SAPO-34 (Sr²⁺), for the capture of CO₂ in confined spaces.^{18,19} Typically, the aforementioned physical adsorbents exhibit a moderate CO₂ heat of adsorption of 45-50 kJ/mol and a recyclable CO₂ uptake of 9-15 cm³(STP)/g (1.7-2.9 wt%) at 1300 ppm. Nonetheless, their overall performance is inadequate and ineffective in the presence of water vapor due to their relative low tolerance to water.

Metal organic frameworks (MOFs), a tunable class of porous solid-state materials, are regarded to offer prospective solutions to various challenges pertaining to gas storage and gas separation.²⁰⁻²⁹ Evidently, the modular and hybrid character of MOFs permit the fine-tuning of their affinity for CO₂, via the introduction of appropriate pre-functionalized ligands and/or the grafting of judiciously selected amine moieties on the open metal sites, and subsequently explore their potential for the CCS.^{22,25-28} Nevertheless, only a limited number of functionalized MOFs, affording the CO₂-chemisorption, showed promise for DAC and low-concentration CO₂ capture from confined spaces (<0.5 %).^{22,26} Outwardly, it was intuited that chemisorption based sorbents are the foremost option for traces CO₂ capture,⁸ and atypically put forward that physical adsorbents are prone to be ineffective for carbon capture at the low CO₂ concentration of 400 ppm due to their plausibly weak interactions with the adsorbed CO₂ molecules. Contradictorily to this uncorroborated assumption, we recently published a series of CO₂-selective MOF adsorbents, namely MSiF₆(pyrazine)₂·2H₂O (referred to as **SIFSIX-3-M** where M = Ni, Cu and Zn), showing excellent CO₂ selectivity and uptake at relatively low CO₂ concentrations using solely the physisorption mechanism,^{17,30,31} and in some instances outclassing some of the amine grafted chemical sorbents.²² Nevertheless, extended exposure of **SIFSIX-3-M** adsorbents to water vapor resulted in an overtime lessening of their associated CO₂ capture capabilities; suggesting their limited prospective deployment to mainly dry conditions.

RESULTS AND DISCUSSIONS

In order to extend the scope of this class of materials, we focused our efforts in better understanding the structure-property of these materials and as a result conceivably adjust/alter their molecular composition to enhance their water stability while maintaining or enhancing their carbon capture capabilities. The ability to construct the looked-for hydrolytically stable MOF with the desired CO₂ adsorption properties will permit its potential use for carbon capture under practical humid conditions, and the subsequent elimination of the costly pre-drying step.

Accordingly, we conducted a structural analysis of the **SIFSIX-3-M** adsorbents with the aim to pinpoint the key

structural features responsible for the noted unique CO₂ capture properties. The key objective is to be able to derive a reasonable structure-property relationship that will assist and guide us in fine-tuning the resultant adsorbent structure to withstand the water vapor and concurrently enhance its intrinsic CO₂ uptake and selectivity at traces CO₂.

Appropriately, close examination of the **SIFSIX-3-M** adsorbents and their respective CO₂ adsorption properties revealed the impact of the periodically aligned fluorine moieties in the contracted square-shaped channels, and that the F...F distance, dictating the channel size, is directly correlated to the strength of the CO₂ interactions with the host framework. Namely, the comparison of **SIFSIX-3-Zn** ($Q_{st} = 45 \text{ kJ. mol}^{-1}$, F...F dist. = 6.784(1) Å), **SIFSIX-3-Ni** ($Q_{st} = 47 \text{ kJ. mol}^{-1}$, F...F dist. = 6.694(1) Å) and **SIFSIX-3-Cu** ($Q_{st} = 54 \text{ kJ. mol}^{-1}$, F...F dist. = 6.483(1) Å) revealed that the CO₂ is more strongly adsorbed at lower concentrations when the size of the square-shaped channel is further contracted, as a result of the shortened distance between the pendant fluorine moieties from diagonally adjacent (SiF₆)²⁻ pillars.^{17,30,31} Considerately, in addition to enabling the MOF pore system characteristics, contracted square-shaped channels with a periodically aligned proximal fluorine moieties, two other parameters were considered for the design and construction of the looked-for hydrolytically stable MOF for carbon capture. Specifically, we elected: i) to employ the Ni(II) as the octahedrally-coordinated metal node since the **SIFSIX-3-Ni** offers a shorter M-F bond distance ($d_{M-F} = 1.99(5) \text{ Å}$)³² then the **SIFSIX-3-Cu** ($d_{M-F} = 2.12(1) \text{ Å}$)¹⁷ and thus prone to express the requisite water vapor tolerance, and ii) to substitute the (SiF₆)²⁻ pillar with an appropriate fluorinated inorganic pillar, offering a relatively stronger coordination bonds and the adequate nucleophilicity that can preclude the observed phase change in the **SIFSIX-3-Cu**, associated with the water molecule introduction within the Cu(II) coordination sphere.³¹

Accordingly, the (NbOF₅)²⁻ was explored as a potential pillar to replace the original inorganic pillar, (SiF₆)²⁻, due its associated distinct attributes: (i) the larger size of Nb⁵⁺ imparts a longer Nb-F bond length (1.899(1) Å) than the Si-F bond (1.681(1) Å), signifying the plausible reduction in the distance between the pendant proximal fluorine moieties within the channel; (ii) the higher nucleophile behavior of the (NbOF₅)²⁻ is anticipated to enhance the water stability of the resultant MOF (Figure 1).

Solvothermal reaction in a hydrofluoric acid aqueous solution containing a mixture of Ni(NO₃)₂·6H₂O, Nb₂O₅ and pyrazine afforded violet square shaped crystals of NiNbOF₅(pyrazine)₂·2H₂O (**1**) which we referred to as **NbOFFIVE-1-Ni**. Single crystal X-ray diffraction (SCXRD) study on a suitable single crystal of **NbOFFIVE-1-Ni** at 296 K revealed that the resultant compound crystallized in a tetragonal space group *I4/mcm* with unit cell parameters $a = b = 9.943(4) \text{ Å}$ and $c = 15.764(6) \text{ Å}$ (Table S1). The purity of the material was confirmed by a full pattern matching using the Le Bail³³ method implemented in Full prof software³⁴ (Figure S1). As anticipated, the **NbOFFIVE-1-Ni** can be regarded as a 3-periodic **pcu**-MOF based on the 2-periodic square grid, Ni(pyrazine)₂, bridged by the (NbOF₅)²⁻ pillars via the axial oxygen and fluorine centers. Each Ni(II) is octahedrally coordinated to four nitrogen centers, from four distinct pyrazine ligands, and one oxygen and one fluorine from the (NbOF₅)²⁻ pillar. It is to note that the assignment of one coordinating

oxygen atom and one coordinating fluorine atom to the two apical positions in the pillar has been observed and validated in similar materials with supporting techniques.³⁵⁻³⁷ As expected, the **NbOFFIVE-1-Ni** encloses a relatively contracted square-shaped channels with a slightly smaller diameter of 3.210(8) Å (derived from the distance between the pendant

fluorine centers, F...F, and by taking account van der Waals radii) then the **SIFSIX-3-Ni** and **SIFSIX-3-Cu** adsorbents (3.694(1) Å and 3.483(1) Å respectively). It is to mention that the Ni...Ni distance (7.030(3) Å) in the 2-periodic square grid, Ni-(pyrazine)₂, is preserved and it is the same in both, the **NbOFFIVE-1-Ni** and **SIFSIX-3-Ni** adsorbents.

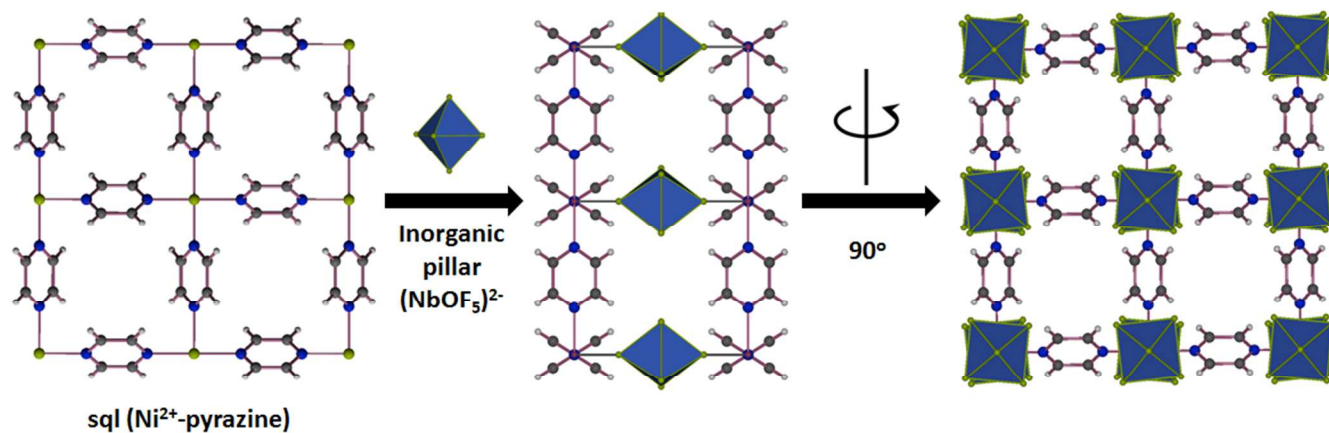


Figure 1. Structural representation of the **NbOFFIVE-1-Ni**: left, the 2-periodic square-grid layer constructed by linking Ni(II) with pyrazine ligands, middle, pillaring of square-grid layers by the $(\text{NbOF}_5)^{2-}$ inorganic pillars, right, square-shaped channels in the resultant 3-periodic **pcu**-MOF, **NbOFFIVE-1-Ni**.

High thermal stability of the material was evaluated by TGA (Figure S5) and variable-temperature powder X-ray diffraction (PXRD) performed in the range of 25 °C to 400 °C, establishing that the material retained its crystallinity over the explored temperature range (Figure S3). Markedly, the hydrolytic stability of the material was confirmed by performing in-situ variable-humidity PXRD (Figure S4) and multiple water adsorption isotherms (Figure S6a) on the **NbOFFIVE-1-Ni**. The exceptional water stability was further confirmed by the conformity of the resultant CO₂ isotherms before and after immersion of material in liquid water for 6 months (Figure S8). Moreover, **NbOFFIVE-1-Ni** showed excellent tolerance to hydrogen sulfide, a feature that is rarely proven for MOFs, as evidenced by the preservation of the material PXRD pattern after exposure to H₂S (Figure S2) and by performing H₂S adsorption isotherms (Figure S6b). It is to state that N₂ adsorption studies performed at 77 K on the activated material indicated as expected that the **NbOFFIVE-1-Ni** doesn't adsorb N₂ at this cryogenic temperature. Conversely, the **NbOFFIVE-1-Ni** adsorbs CO₂ and accordingly this probe was employed to evaluate the porosity properties of this adsorbent. Specifically, the apparent surface area and the pore volume were derived from the CO₂ adsorption isotherm at 273 K (Figure 2b) and estimated to be 280 m²/g and 0.095 cm³/g, respectively. Distinctly, the **NbOFFIVE-1-Ni** provided the expected high affinity for CO₂ at low concentrations as evidenced by the steepness in the CO₂ adsorption isotherm and the attainment of the plateau at relatively very low CO₂ pressures (Figure 2a, S7).

Detailed analysis of the CO₂ adsorption isotherms associated to the **NbOFFIVE-1-Ni** and their comparison with a closely related material, **SIFSIX-3-Ni**, revealed an enhancement in the CO₂ heat of the adsorption (Figure 2d) and most importantly a noticeable increase in the CO₂ volumetric uptake at 400 ppm of nearly 340%. This remarkable CO₂ uptake improvement, synonym of enhanced CO₂-framework interac-

tions, is directly correlated to the closer proximity of the pendant fluorine centers, decorating the square-shaped channels, in the case of the **NbOFFIVE-1-Ni** with an F...F distance of 3.210(8) Å as compared to the 3.694(1) Å distance in the case of the **SIFSIX-3-Ni**.

Significantly, the **NbOFFIVE-1-Ni** adsorbent offers an even higher CO₂ volumetric uptake at 400 ppm than the best material so far for carbon capture at traces CO₂ using physisorption mechanism, namely **SIFSIX-3-Cu** (Figure 2c). Precisely, the **NbOFFIVE-1-Ni** adsorbs a 51.4 cm³/cm³ (1.3 mmol/g) of CO₂ at 400 ppm and 298 K as compared to a 44.6 cm³/cm³ for the **SIFSIX-3-Cu**, equivalent to a 15% increase than the best reported physical adsorbent to the best of our knowledge. In view of that, the **NbOFFIVE-1-Ni** can be regarded as the best physical adsorbent material for carbon capture at very low concentration of CO₂ (traces) with the highest CO₂ gravimetric and volumetric uptakes, driven mainly by physisorption mechanism. Excellent stability and the relatively mild condition for regeneration of the material also contribute to its prominence over other materials. The preeminent carbon capture potential of the **NbOFFIVE-1-Ni**, at 400ppm of CO₂, is even magnified at higher temperatures where the **NbOFFIVE-1-Ni** adsorbed the equivalence of an additional 63% more CO₂ at 400 ppm and 328 K than the **SIFSIX-3-Cu** adsorbent. It is to state that the volumetric uptake for well-known MOFs such as Mg-MOF-74 is comparatively very small at 400 ppm (≈ 1.7 cm³/cm³). In terms of gravimetric uptake both **NbOFFIVE-1-Ni** and **SIFSIX-3-Cu** have similar CO₂ capacities and adsorb an equivalent of 43 cm³STP/g at 1300 ppm and 298 K. This gravimetric uptake amounts to a notable 300% increase than the SAPO-34 (Sr²⁺), the reference physical adsorbent for the CO₂ removal in a long-duration crewed space exploration missions. Recently, a copper silicate (SGU-29) was reported to show a CO₂ volumetric uptake of 26 cm³/cm³ and 40 cm³/cm³ at CO₂ concentrations of 400 and 1000 ppm (single gas adsorption), respectively.³⁸ Noticeably, the CO₂ volumetric and gravimetric

uptakes of this purely inorganic CO₂-adsorbent are much lower than **NbOFFIVE-1-Ni** at very low CO₂ pressures.

In order to gain a better insight on the structure-property relationship leading to the unusually strong physisorption of CO₂ and the subsequent improvement in the CO₂ adsorption capabilities of the **NbOFFIVE-1-Ni**, we succeeded in solving the

crystal structure of the **NbOFFIVE-1-Ni** in the presence CO₂ and most importantly localized the adsorbed CO₂ molecules. Purposely, we collected a SCXRD data on a degassed crystal of **NbOFFIVE-1-Ni** under 1 bar dry CO₂ atmosphere at 298 K. The structure containing CO₂ molecules was solved in

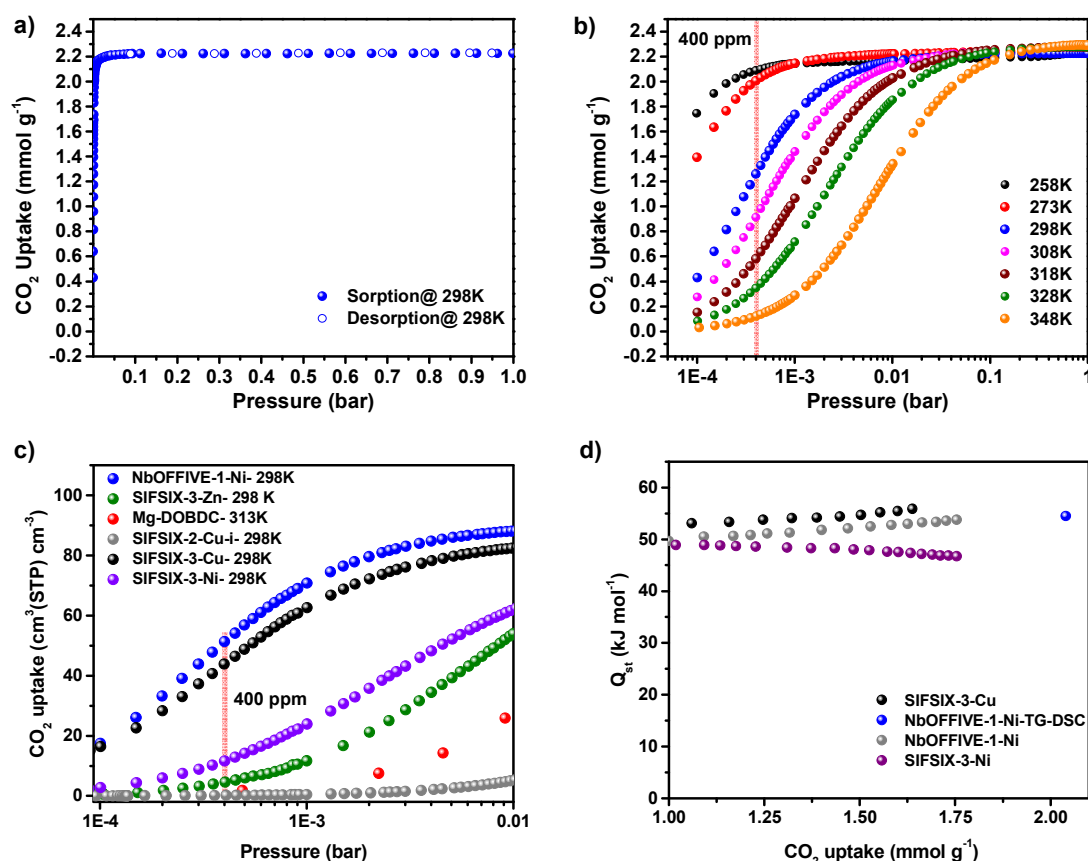


Figure 2. a) CO₂ adsorption isotherm for **NbOFFIVE-1-Ni** up to 1 bar and 298 K. b) CO₂ adsorption isotherms for **NbOFFIVE-1-Ni** at different temperatures. c) Comparison of the CO₂ uptake at low pressures between the **NbOFFIVE-1-Ni** and the **SIFSIX** family as well as the **Mg-MOF-74**, one of the best MOF for low pressure CO₂ adsorption. d) CO₂ heat of adsorption for **NbOFFIVE-1-Ni** as compared to **SIFSIX-3-Ni** and **SIFSIX-3-Cu**, determined using multiple CO₂ adsorption isotherms as well as TG-DSC measurements.

the same space group as the as-synthesized compound, hosting water molecules, namely a tetragonal space group *I4/mcm* with unit cell parameters $a = b = 9.903(1)$ Å and $c = 15.720(2)$ Å and formulated as $\text{NiNbOF}_5(\text{pyrazine})_2 \cdot 0.84(\text{CO}_2)$ (**2**) (Table S2).

The interpretation of the Fourier difference data allows us to clearly localize the CO₂ molecules within the square-shaped channels of the **NbOFFIVE-1-Ni**. 0.84CO_2 structure. Interestingly, the CO₂ molecule occupy a high energetically favorable position, where the electropositive carbon of the CO₂ is surrounded by four electronegative fluorine centers from four distinct (NbOF₅)²⁻ pillars (F...C_{CO2} distance = 3.050(8) Å) and the electronegative oxygen atoms of the CO₂ are surrounded by pyrazine hydrogens (C-H...O distance = 2.99 Å, angle = 117°) as depicted in Figure 3. It is worth to mention that the F...C_{CO2} distance (ca. 3.050(8) Å) in the case of the **NbOFFIVE-1-Ni**. 0.84CO_2 is less than the sum of the C and F van der Waals radii, supporting the CO₂ molecules strong in-

teractions with the host framework. These interactions are relatively stronger than those observed in the case of the **SIFSIX-3-Ni**, structure derived from the PXRD data, where the distance F...C_{CO2} is found to be equal to 3.302 Å,³² a distance clearly larger than the C and F van der Waals radii and confirming the relatively weaker CO₂-framework interactions than in the case of the CO₂ adsorbed in the **NbOFFIVE-1-Ni** adsorbent.

It can be inferred from the crystal structure that the presence at close proximity of relatively strong and concurrent complementary interactions created an ideal and energetically favorable 'sweet spot' for the adsorption of CO₂, and proffered unique CO₂ capture features to the **NbOFFIVE-1-Ni** adsorbent. The presence of highly favorable CO₂-framework interactions in case of **NbOFFIVE-1-Ni** is also evidenced by the steady and marked high CO₂ heat of adsorption (Figures 2d, S12). The CO₂ heat of adsorption for the **NbOFFIVE-1-Ni** was determined using CO₂ adsorption isotherms at variable

temperature (Figure 2b and S7) and further supported by the direct TG-DSC measurement (Figure 2d, S12).

In order to assert the potential of the **NbOFFIVE-1-Ni** as a proper physical-adsorbent for carbon capture at dilute CO₂ concentrations, we performed mixed-gas experiments under conditions akin to the real world carbon capture in confined spaces or from ambient air. A series of cyclic CO₂ (1%)/N₂ (99%) column breakthrough experiments at 298 K were performed in the presence and absence of water vapor (both dry and humid conditions) (Figure 4). The breakthrough time under dry conditions for a 1% CO₂ in the gas stream with the flow rate of 10 cc/min revealed a remarkable retention of 415 min/g that is equivalent to the adsorbed CO₂ equaling 8.2 wt%.

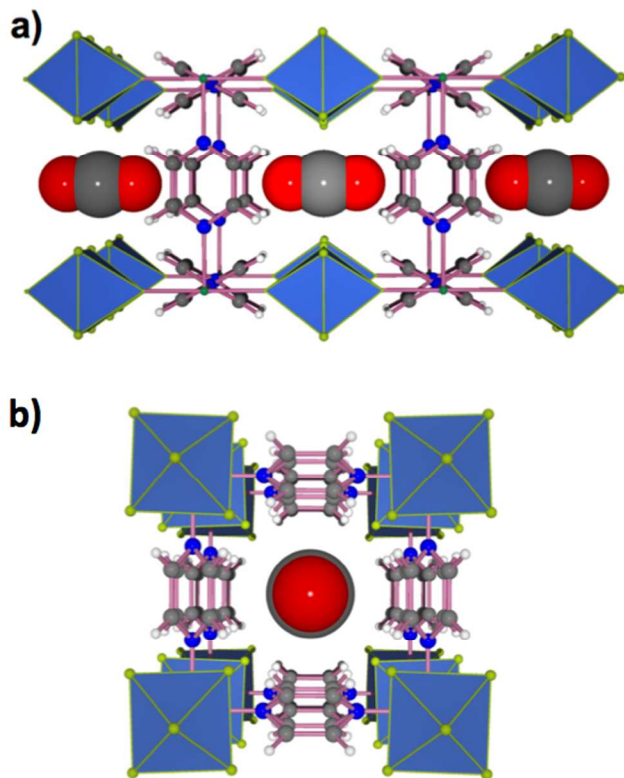


Figure 3. Direct visualization of CO₂ molecules inside the crystal structure of the **NbOFFIVE-1-Ni** highlighting the highly favorable arrangement of the CO₂ molecules within the contracted square-shaped channels along [010] and [001].

Certainly, the presence of humidity (75%RH) did not significantly alter the CO₂ breakthrough time (283 min/g, uptake of 5.6 wt%). In addition, the CO₂ uptakes in dry and humid streams were conserved as proven by the reproducible data from multiple cycle breakthrough experiments, where prior to each new cycle the adsorbent was fully reactivated at 378 K (Figure S10, S11). Interestingly, the water vapor was retained in the column for 680 min/g which is equivalent to a water uptake of 13.8 wt%. It is to state that the noticeable adsorbed water uptake did not jeopardize the carbon capture capabilities of the **NbOFFIVE-1-Ni** and suggests a rare simultaneous adsorption of water and CO₂ in contrast to most MOFs and zeolites. Appropriately, column breakthrough experiments for very dilute CO₂ concentrations (i.e. 1000 ppm CO₂), with a

flow rate of 20 cm³/min, showed that CO₂ is retained in the column for 1880 min/g with an equivalent uptake of 7.4 wt % (Figure S9).

Finally, in order to position the carbon capture performance of the **NbOFFIVE-1-Ni** vis-à-vis the existing technologies, and in comparison with key benchmark materials (both chemical and physical adsorbents) deployed in real-world applications or regarded to offer great promise, we compiled and assessed each material CO₂ removal capacity at around 1000 ppm CO₂ for 1 day against the given material associated CO₂ heat of adsorption. For practical reasons we assumed that all sorbent are fully recyclables with the exception of the lithium hydroxide (LiOH), a non-recyclable sorbent.³⁹

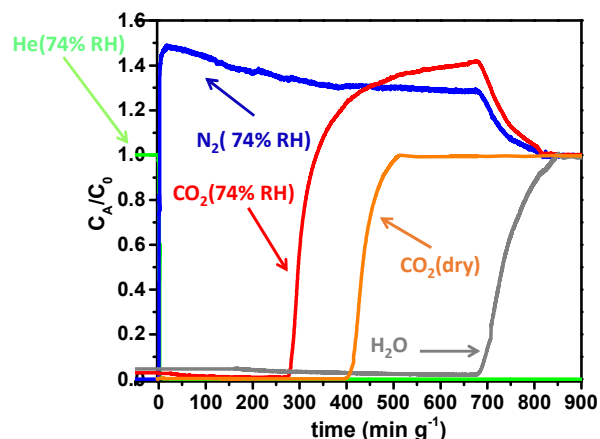


Figure 4. Column breakthrough tests for the **NbOFFIVE-1-Ni** with the mixed-gas CO₂/N₂ (1%/99%) at 1 bar and 298 K in both dry and humid conditions (10 cm³/min flow rate).

For comparison purposes, we arbitrarily fixed and adopted the full adsorption-desorption cycle to be at 60 min (24 cycles a day) and the evaluation based on the requirements for the CO₂ scrubbing in confined spaces, specifically 1 kg of CO₂ captured per day and per person.

Interestingly, as depicted in Figure 5, the **NbOFFIVE-1-Ni** exhibits the best compromise between the carbon capture capacity and the required heat for regeneration. Precisely, at 1000 ppm CO₂, the **NbOFFIVE-1-Ni** offers the highest CO₂ capacity in 1 day (24 cycles) associated with the optimal heat of adsorption (dictating the required energy for regeneration) than all the evaluated sorbents such as LiOH, liquid amine, amine supported solids, zeolites 5A (Ca²⁺), SAPO-34 (Sr²⁺) and the recently reported copper silicate (SGU-29). The CO₂ uptake at 1000 ppm (kg.kg⁻¹.day⁻¹) was calculated from mixed gas breakthrough experiment for the **NbOFFIVE-1-Ni** adsorbent and from the reported adsorption isotherms or reported data for other materials. It is to be noted that CO₂ uptake obtained from dynamic conditions such as breakthrough adsorption column is always slightly lower than CO₂ uptake obtained from adsorption isotherms (equilibrium condition). These values, associated to one cycle, were multiplied by 24 (1 hour cycle) in order to obtain a given material daily performance and derive a relative comparison between evaluated materials per one day.

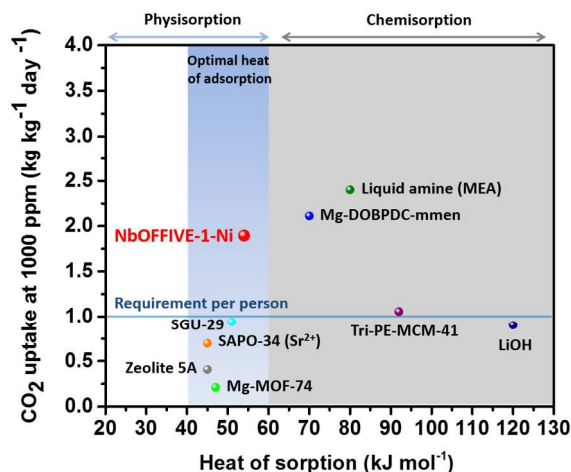


Figure 5. Heat of adsorption- CO_2 uptake (at 1000 ppm for 1 day) trade-off for **NbOFFIVE-1-Ni** as compared to benchmark and newly developed materials. At the exception of LiOH, the CO_2 uptake for 1 day for all the materials was calculated assuming a 60 min adsorption-desorption cycle.

Evidently, although this is a simplified analysis, assuming 24 cycles per day and not taking into account the rate of CO_2 adsorption/desorption and many other constraints relevant to real processes, particularly for amine supported materials and chemical sorbents,^{14,40} it portrays and places the **NbOFFIVE-1-Ni** as a prospective physical-adsorbent for an effective and energy-efficient CO_2 capture in confined spaces and from atmospheric air.

Work is in progress to assess the related economics and technicalities associated with the potential deployment of the **NbOFFIVE-1-Ni** adsorbent in practical carbon capture applications from atmosphere and in confined spaces using rapid thermal swing adsorption.

CONCLUSIONS

In summary, the close examination of the structural features of the **SIFSIX** adsorbent family permitted the election of a bulkier and a relatively nucleophilic inorganic pillar, namely the $(\text{NbOF}_5)^{2-}$ instead of the original $(\text{SiF}_6)^{2-}$ pillar, and the successful practice of reticular chemistry for the construction a hydrolytically stable **pcu-MOF**, **NbOFFIVE-1-Ni**, with contracted square-channels decorated with proximal fluorine moieties and ideal for carbon capture at very dilute CO_2 concentrations. To the best of our knowledge, the reported **NbOFFIVE-1-Ni** stands as the best physical-adsorbent material for CO_2 capture from atmospheric and confined spaces, driven mainly by physical adsorption. Specifically, in terms of the CO_2 adsorption energetics and uptakes, the **NbOFFIVE-1-Ni** has the highest uptake for CO_2 at 400 ppm with associated relatively optimal energy for regeneration. From the perspective of the carbon capture in a confined space, air removal viewpoint, the **NbOFFIVE-1-Ni** offers a 300 % higher CO_2 gravimetric and volumetric uptakes than the SAPO-34 (Sr^{2+}), the reference physical adsorbent for the CO_2 removal in a long-duration crewed space exploration missions, with equivalent CO_2 adsorption energetics.

Direct observation and localization of the adsorbed CO_2 molecules within the adsorbent channels, using single crystal X-ray

diffraction data, gives valuable insights on the nature of the CO_2 -framework interactions governing the high affinity of the **NbOFFIVE-1-Ni** for CO_2 even at very dilute concentrations. This unique structural insight will certainly pave the way to the design and the construction of new and practical physical adsorbents with a similar CO_2 affinity and a further improved CO_2 uptake. Practically, unlike many other MOFs, the **NbOFFIVE-1-Ni** offers great potential to be easily synthesized in large quantities (g to kg) and in a cost-effective manner; and thus placing this physical adsorbent in the right track for large-scale deployment and plausible commercialization. Work is in progress to scale-up and test this MOF at a pilot scale.

EXPERIMENTAL SECTION

Materials and methods.

Elemental Analyses for C, H and N were carried out on a ThermoFinnigan Apparatus. Thermal gravimetric analyses (TGA) were performed under N_2 flow (25 ml/min) with a heating rate of $5^\circ\text{C}/\text{min}$ using a TA Q500 apparatus. Enthalpy of adsorption for CO_2 and H_2O was measured using SENSYS evo TG-DSC from Setaram Instrumentation that can carry out simultaneous high resolution DSC and TGA experiments. In a typical experiment, the sample was activated in-situ at 105°C under continuous dry N_2 flow at the rate of 15 ml/min. For sorption experiment, baseline was obtained under dry N_2 flow at the rate of 15 ml/min at 25°C . CO_2 or humid N_2 was connected at auxiliary gas port and gas was changed from N_2 to CO_2 / humid N_2 exactly after 1 hour and TGA and DSC signal were monitored for few hours to obtain uptake and heat of sorption respectively. The powder X-ray diffraction patterns and the variable humidity powder X-ray diffraction patterns (VH-PXRD) were collected over the 2θ range $4-40^\circ$ on a high resolution PANalytical X'Pert MPD-PRO diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV/40 mA). Variable Temperature Powder X-ray Diffraction (VT-PXRD) patterns measurements were collected on a PANalytical X'Pert MPD-PRO X-ray diffractometer equipped with an Anton-Parr CHC+ variable temperature stage. Measurements were performed at 45 kV, 40 mA for $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) with a scan speed of $1.0^\circ/\text{min}$ and a step size of 0.02° in 2θ . Samples were placed under vacuum during analysis and the sample was held at the designated temperatures for at least 15 minutes between each scan.

Synthesis of NbOFFIVE-1-Ni

All reagents were used as received from commercial suppliers without further purification: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros), Nb_2O_5 (Aldrich), Pyrazine (Aldrich), HF (Aldrich). Pyrazine (384.40 mg, 4.80 mmol), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (174.50 mg, 0.60 mmol), Nb_2O_5 (79.70 mg, 0.30 mmol) and $\text{HF}_{\text{aq}} 48\%$ (0.26 ml, 7.15 mmol) were mixed in a 20ml Teflon liner. The mixture was diluted with 3 ml deionized water and then the autoclave was sealed and heated to 130°C for 24h. After cooling down the reaction mixture to room temperature, the resultant violet square-shaped crystals, suitable for single crystal X-ray structure determination, were collected by filtration, washed with ethanol and dried in air. Elemental analysis: N%: 11.88 (theo: 12.21), C%: 20.58 (theo: 20.54), H%: 2.54 (theo: 2.64), O%: 11.42 (theo: 10.46). $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_4\text{F}_5\text{NiNb}$ $\text{NiNbOF}_5(\text{pyr})_2 \cdot (\text{H}_2\text{O})_2$ (called **NbOFFIVE-1-Ni**) was activated at 105°C for 12 hours under high vacuum (3milliTorr) before each adsorption experiment.

ASSOCIATED CONTENT

Supporting Information

PXRD, additional structural figures, sorption, and single-crystal X-ray diffraction data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interests.

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CO₂ physisorption as the new effective and efficient path for traces CO₂ removal: A deliberately designed hydrolytically stable MOF, **NbOFFIVE-1-Ni**, was found to possess the highest CO₂ volumetric and gravimetric uptake at 400 ppm for any physical adsorbents.

