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Hydrocarbon recovery using ultra-microporous fluorinated MOF platform with and without uncoordinated metal sites: I- Structure properties relationships for C₂H₂/C₂H₄ and CO₂/C₂H₂ separation

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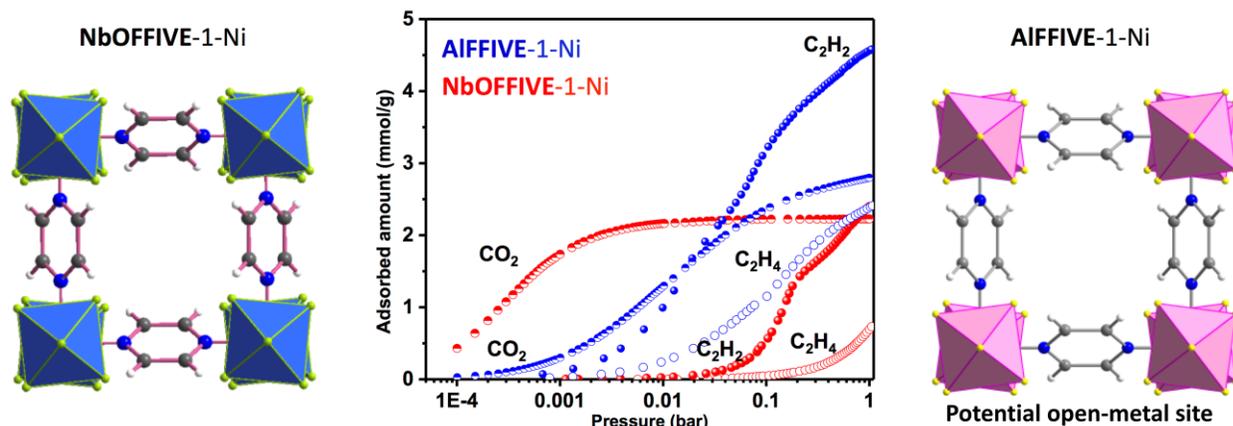
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Highlights

- Stable fluorinated Metal Organic Frameworks with tunable structural properties;
- Structural properties of **MFFIVE**-1-Ni with relation to C₂₊ adsorption were unveiled;
- Substitution of Nb⁵⁺ by Al³⁺ led to improved separation for C₂H₂/C₂H₄:1/99 system;
- **NbOFFIVE**-1-Ni shows unprecedented CO₂/C₂₊ selectivity in favor of CO₂;
- Substitution of Nb⁵⁺ by Al³⁺ affects the mechanism involved in C₂₊ separations;

Graphical abstract



(Two fluorinated ultra-microporous materials, **NbOFFIVE-1-Ni** and **AIFFFIVE-1-Ni** with $[\text{NbOF}_5]^{2-}$ and $[\text{AlF}_5]^{2-}$ building block acting as inorganic pillars, respectively, result in much different adsorption behavior for CO_2 and C_2 . **NbOFFIVE-1-Ni** with confined pore space exhibit much higher CO_2 uptake amount at low pressures, by contrast, **AIFFFIVE-1-Ni** with potential open metal sites in pore spaces exhibit relatively larger pore volume, leading to enhanced C_2H_2 adsorption performance at low pressures and improved $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation selectivity.)

Abstract

In this work, the reticular chemistry approach was implemented on a very stable ultra-microporous fluorinated **MFFIVE-1-Ni** MOFs to unveil the effect of subtle changes of the structure-employment of different fluorinated inorganic block on the adsorption of C_2H_2 , C_2H_4 and CO_2 . A series of variable temperature single C_2H_2 , C_2H_4 and CO_2 adsorption isotherms and mixed gas adsorption column breakthrough experiments for different $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and $\text{CO}_2/\text{C}_2\text{H}_2$ gas pair systems were carried out on the two isorecticular **NbOFFIVE-1-Ni** and **AIFFFIVE-1-Ni**, containing respectively $[\text{NbOF}_5]^{2-}$ and $[\text{AlF}_5]^{2-}$ inorganic building blocks. The introduction of potential open metal site in a very confined pores led to favoring interaction of C_2H_2 but lowering the interaction with CO_2 , which resulted in enhancement of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$

selectivity at low C_2H_2 concentration but a decrease in CO_2/C_{2+} selectivity. The comparison of the C_2H_2/C_2H_4 and CO_2/C_2H_2 separation performances with the structures of the **MFFIVE-1-Ni** MOFs provides useful information to shed light on the relationship between the structural features of this MOF platform and C_2H_2/C_2H_4 and CO_2/C_2H_2 separation properties. This is a critical step in the wanted rational discovery/design of materials with enhanced performances for C_2H_2 recovery from C_2H_4 and CO_2 at different concentration and having different level of input energy for recycling.

Keywords: Metal-organic frameworks (MOFs), Fluorinated MOFs, ultra-microporous MOFs Hydrocarbon recovery, CO_2 removal from hydrocarbon.

1. Introduction

Ethylene (C_2H_4) is the largest industrially produced hydrocarbon with a worldwide production of 150 million tons in 2016 [1]. Acetylene is a byproduct of ethylene production processes (pyrolysis of hydrocarbons, which is the thermal cracking of petrochemicals in the presence of steam) and it acts as a poison to the catalysts used for making polyethylene out of the ethylene product. Ethylene to be used for polymerization processes has to be 99.90% pure. This is known as polymer-grade ethylene and the maximum allowable limit of acetylene should not be higher than 5 ppm [2].

Purification of C_2H_4 to produce different grade of polymer grade polyethylene is a multistep process that requires different separation/purification stages depending on the composition of the feedstock. Gas sources for ethylene contain C_2H_6 , C_2H_2 and other impurities and must undergo complex/multistep, often energy inefficient separation, such as cryogenic distillation or catalytic separation [3]. This treatment can take various routes,

depending on the acetylene content and whether or not high-purity acetylene recovery is needed. There are two main paths; extract the acetylene from the C_2 -stream and recover it as a product, or convert it into useful product such as ethylene. Each path involve different unit operations, which affect in turn the overall process sequence. In general, C_2H_2 is removed by using two main processes; (i) Recovery through Solvent Extraction and (ii) conversion to ethylene via catalytic hydrogenation system [4-5]

In the quest to reduce the energy footprint, several studies at the laboratory scale showed good separation via ultra-microporous MOFs, acting as separation agents (both uptake and C_2H_2/C_2H_4 selectivity). This is particularly valid for MOFs where the very confined pore play a major role in maximizing the synergy between thermodynamic and kinetic effects [6-11], resulting to high selective separation agents for C_2H_2 or CO_2 . This is evident from the evolution of the adsorptive uptake C_2H_2/C_2H_4 and CO_2/C_2H_4 ratios [8], largely favorable for ultra-microporous materials [6-11, 25]

The first complexity in purification of C_2H_4 is the presence of different concentrations for C_2H_6 , CO_2 and C_2H_2 where only ppm level of C_2H_2 is present. Accordingly, the search for materials that interact relatively strongly with C_2H_2 is of prime importance to favor further the selective removal of C_2H_2 at very low concentration. Although the removal of C_2H_2 from C_2H_4 is less complicated than the removal of C_2H_4 from C_2H_6 , nevertheless, the highly diluted amount of C_2H_2 elevate the degree of complexity of this gas separation system. With this regards, only fluorinated MOFs having diverse organic building blocks were studied for C_2H_2/C_2H_4 separation [6-11] and no insights were reported on the rational effect of uncoordinated metal sites, via inorganic pillars substitution. The other complexity

in hydrocarbon recovery in general and C_2H_2 , C_2H_4 and C_2+ in particular, is the selective removal of CO_2 in the presence of highly polarizable molecules. The general tendency is that all class of materials including MOFs adsorb hydrocarbons such as C_2H_2 , C_2H_4 , C_3H_8 and C_4H_{10} much strongly than CO_2 ; this is unpractical because CO_2 is highly diluted in relevant gas streams and gas processing necessitate rather CO_2 selective materials.

In this work, we report a rare structural modification in ultra-microporous fluorinated MOFs via introduction of open metal sites in highly confined pores. The combination of these structural features led to drastic enhancement of C_2H_2 selectivity vs C_2H_4 in highly desirable diluted conditions for C_2H_2 removal applications. Furthermore, the confined pore system of this fluorinated MOF without open sites afforded a high CO_2 selectivity vs. highly polarizable gas molecules.

2. Materials and methods

The fluorinated MOFs **NbOFFIVE**-1-Ni (apparent surface area $280\text{ m}^2/\text{g}$, estimated pore volume $0.095\text{ cm}^3/\text{g}$) and its isomorph **AlFFIVE**-1-Ni (apparent surface area $258\text{ m}^2/\text{g}$, estimated pore volume $0.102\text{ cm}^3/\text{g}$) are derived from the **SIFSIX** family [12-13] and can be described as the pillaring of $M'(II)$ -pyrazine square-grid layers with $[NbOF_5]^{2-}$ or $[AlF_5(H_2O)]^{2-}$ inorganic building block, respectively [14-18]. Detailed description of synthesis, characterization and experimental techniques are given in Supplementary Information file.

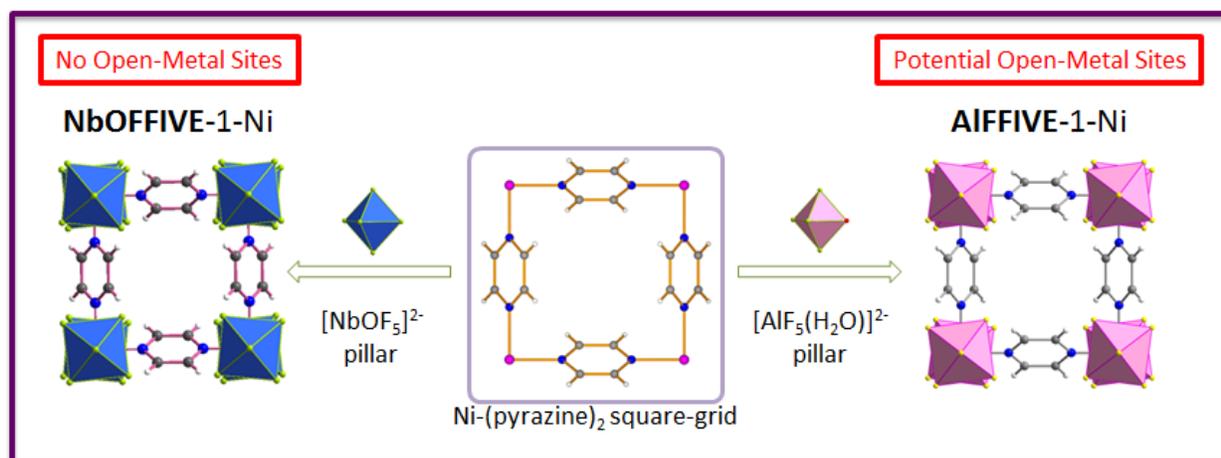


Figure 1. Schematic showing the subtle difference in the crystal structures of **NbOFFIVE-1-Ni** and **AIFFFIVE-1-Ni-1**

3. Results and discussion

Understanding the structure adsorption-property relationship is a key element to develop better separation agents for complex separations [19-24]. The main differences between the two employed structures (Figure 1) is the presence of uncoordinated Al³⁺ site in case of **AIFFFIVE-1-Ni**, thus, offering the opportunity for molecules to interact with fluorine and the open metal sites in very confined pore environment. While in the case of **NbOFFIVE-1-Ni** only interaction with fluorine is available for molecules in the same highly confined pore environment. Furthermore, the presence of bulkier [NbOF₅]²⁻ or [AlF₅(H₂O)]²⁻ implies a pyrazine ring tilting not accessible in **SIFSIX-3-Ni** structure, thus leading to a contracted pore window. **AIFFFIVE-1-Ni** exhibits relatively higher pore volume due to the presence of [AlF₅]²⁻ inorganic pillar (after activation) and provide higher capture amount for hydrocarbons than **NbOFFIVE-1-Ni**. These subtle differences in the intrinsic structural features demonstrated very interesting properties for separation and sensing of CO₂, H₂O,

H₂S and SO₂ [14-18, 25-26]. Most importantly, **NbOFFIVE-1-Ni** was found to adsorb C₃H₆ and exclude fully C₃H₈ while very poor C₃H₆/C₃H₈ selectivity was observed for **AlFFIVE-1-Ni**, in addition both **NbOFFIVE-1-Ni** and **AlFFIVE-1-Ni** exhibit extremely high hydrolytic stability and can capture CO₂ and water concurrently with high selectivity [17] but with different performances at different operation conditions.

To explore further the structure-separation properties relationship of this fluorinated MOF platform, we found it compelling to study the adsorption of acetylene (C₂H₂), the smallest hydrocarbon molecules with the same kinetic diameter as CO₂, and analyze the differences in the performances of these two isostructural MOFs for the adsorptive separation of C₂H₂/C₂H₄ and C₂H₂/CO₂.

In order to perform an initial assessment, single C₂H₂ and C₂H₄ adsorption measurements were performed at 298K (Figure 2). Interestingly, C₂H₄ is barely adsorbed on **NbOFFIVE-1-Ni** at low pressure with an uptake of ca. 0.7 mmol/ at 1 bar, while **AlFFIVE-1-Ni** adsorbs C₂H₄ with a significant amount of 1.15 and 2.4 mmol/g at 0.1 and 1 bar, respectively. These results are also confirmed using the gravimetric technique at low and high pressure (Figure S1). Adversely, both compounds adsorb significant amount of C₂H₂ but with different uptakes at low pressure and atmospheric pressure. This is in turn reflected in a much steeper C₂H₂ adsorption isotherm (as compared to C₂H₄) for **AlFFIVE-1-Ni** with an uptake of ca 1.0, 3.2 and 4.6 mmol/g vs ca. 0.023, 0.58 and 2.4 mmol/g for **NbOFFIVE-1-Ni**, respectively at 0.01, 0.1 and 1 bar.

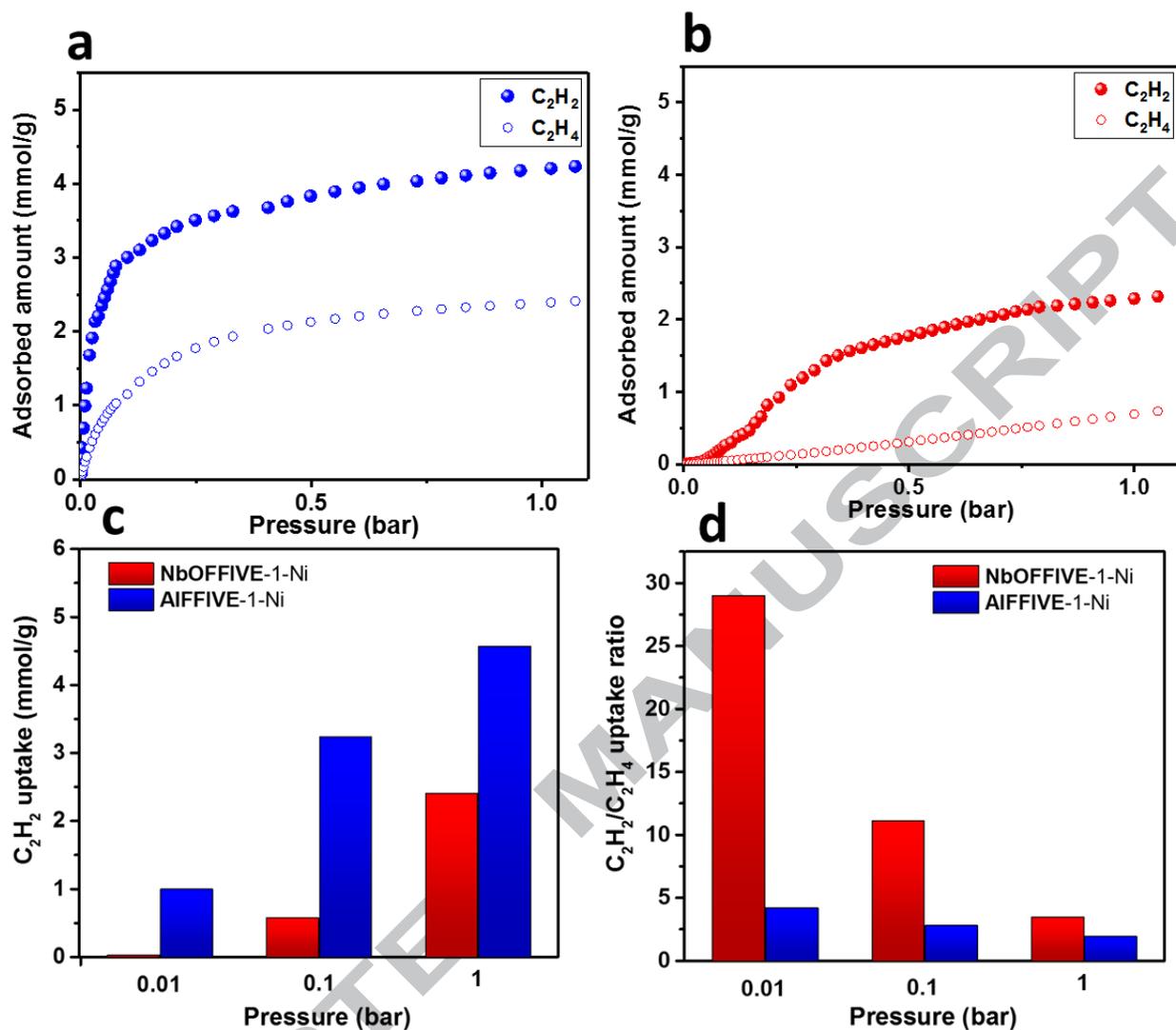


Figure 2. C_2H_2 and C_2H_4 single gas adsorption isotherms on (a) AIFIVE-1-Ni and (b) NbOFFIVE-1-Ni at 298 K. (c) C_2H_2 uptake at various pressures and (d) C_2H_2/C_2H_4 uptake ratio calculated from single gas adsorption isotherms at 298K.

Interestingly, initial performance evaluation based on single gas adsorption shows that the C_2H_2/C_2H_4 uptake ratio (Figure 2d) is high for NbOFFIVE-1-Ni but at the expense of C_2H_2 low uptake. The high uptake ratio particularly at 0.01 bar is explained by the difficulty for C_2H_4 to diffuse into the pore at such low pressure. Adversely, the substitution of $[NbOF_5]^{2-}$ by the $[AlF_5]^{2-}$

inorganic pillar led to relatively more open structure having uncoordinated metal sites. These combined effects resulted in relatively better accessibility to the pores for C_2H_2 and C_2H_4 and much stronger interactions in the pore with much higher C_2H_2 uptake even at 0.01 bar (1 mmol/g). In light of the difference in the steepness of C_2H_2 adsorption particularly at low pressure, we aimed to assess the effect of introduction of open metal sites, from the adsorbates-adsorbents interaction point of view. Accordingly variable temperature adsorption isotherms (Figure S2-S3) of C_2H_2 and C_2H_4 at 273, 298 and 313K were used to calculate the isosteric heat of adsorption (Figure 3). Interestingly, substitution of $[NbOF_5]^{2-}$ inorganic pillar by $[AlF_5]^{2-}$, led to an enhancement from 34 to 38 kJ/mol for C_2H_2 and from 25 to 31 kJ/mol for C_2H_4 . Therefore, the jointly increased heat of adsorption seems at this stage of study to be detrimental for improving the selectivity and facilitation of recyclability. The variable temperature adsorption isotherms for CO_2 for both compounds, as reported elsewhere [16] are shown Figure S4. Comparison of CO_2 adsorption data at 298K on both compounds against the corresponding data for C_2H_2 and C_2H_4 is shown in Figure S5.

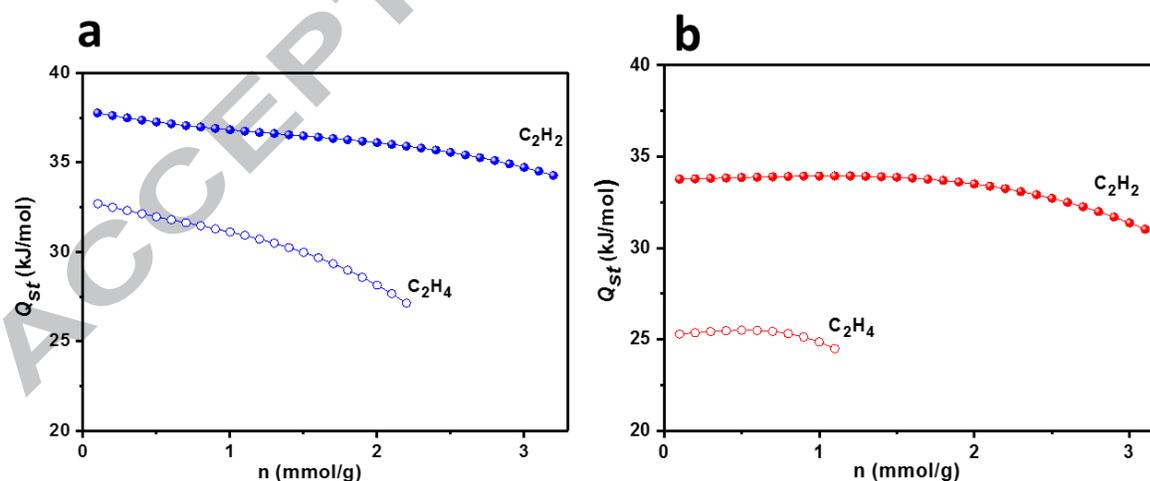


Figure 3. Heat of C_2H_2 and C_2H_4 adsorption for **AlFIVE-1-Ni-1** (a) and for **NbOFFIVE-1-Ni** (b)

In light of the almost negligible adsorption of C_2H_4 as compared to C_2H_2 in case of **NbOFFIVE-1-Ni** and the enhancement of C_2H_2 and C_2H_4 uptake in case of **AlFFIVE-1-Ni-1**, we opted to evaluate the separation performance of these two compounds for C_2H_2/C_2H_4 separation in two cases (i) when C_2H_2 is in bulk amount in the gas feed and (ii) when it is diluted, the latter case is most common scenario in the real application. Remarkably, C_2H_2/C_2H_4 :50/50 adsorption column breakthrough experiment (Figure 4) showed that **NbOFFIVE-1-Ni** retain 50% more C_2H_2 than **AlFFIVE-1-Ni**, while C_2H_4 is 50% less retained in **NbOFFIVE-1-Ni**. This result indicated that when bulk amount of C_2H_2 is present in the feed, **NbOFFIVE-1-Ni** is more selective due to the molecular sieving effect in good agreement with the single adsorption data showing small uptake for C_2H_4 . Conversely, the high Q_{st} for C_2H_2 and C_2H_4 in case of **AlFFIVE-1-Ni**, make the co-adsorption highly competitive between C_2H_2 and C_2H_4 , thus triggering less selective separation toward C_2H_2 at equivalent mixture of C_2H_2 and C_2H_4 . Increasing the flow from $1\text{ cm}^3/\text{min}$ to $2\text{ cm}^3/\text{min}$ did not affect the performance of the compounds (Figure S6). These results were compared the best reported MOFs in terms of C_2H_2 , C_2H_4 uptakes and their corresponding C_2H_2/C_2H_4 selectivity, calculated using IAST (Figure S7, S8, S9).

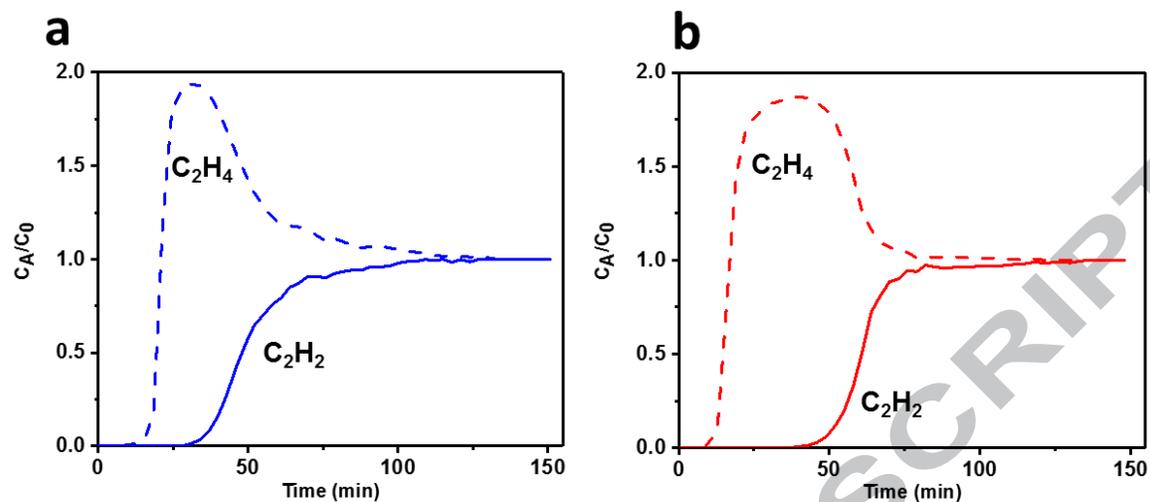


Figure 4. Column breakthrough tests **AIFFIVE-1-Ni** (a) **NbOFFIVE-1-Ni** (b) and (red) with $C_2H_2/C_2H_4:50/50$ at 298 K and 1 bar total pressure ($1 \text{ cm}^3/\text{min}$ flow rate).

Further, we opted to test the performance of both compounds when the C_2H_2 diluted in the C_2H_2/C_2H_4 mixture. The aim of this investigation is to explore the effect of C_2H_2 interaction enhancement between the two isostructural compounds. Delightfully, in spite of the competition with C_2H_4 , **AIFFIVE-1-Ni** was found to retain more selectively C_2H_2 than its isostructural analogue using $C_2H_2/C_2H_4:1/99$ mixtures. These results give a clear indication that enhancement of C_2H_2 interactions is key for purification applications where C_2H_2 is present in small concentrations. Thus, an isostructural analogue combining the favorable C_2H_2 thermodynamics of adsorption like **AIFFIVE-1-Ni** and favorable C_2H_2 diffusion like **NbOFFIVE-1-Ni** will be beneficial to enhance further the separation efficiency toward C_2H_2 in diluted conditions.

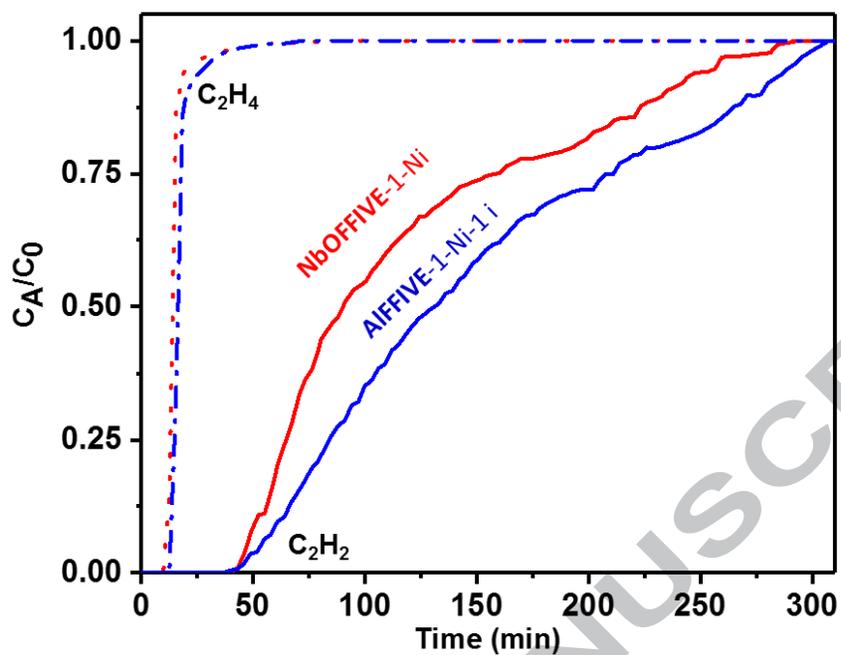


Figure 5. Column breakthrough tests NbOFFIVE-1-Ni and AIFIVE-1-Ni with C₂H₂/C₂H₄:1/99 at 298 K and 1 bar total pressure (1 cm³/min flow rate).

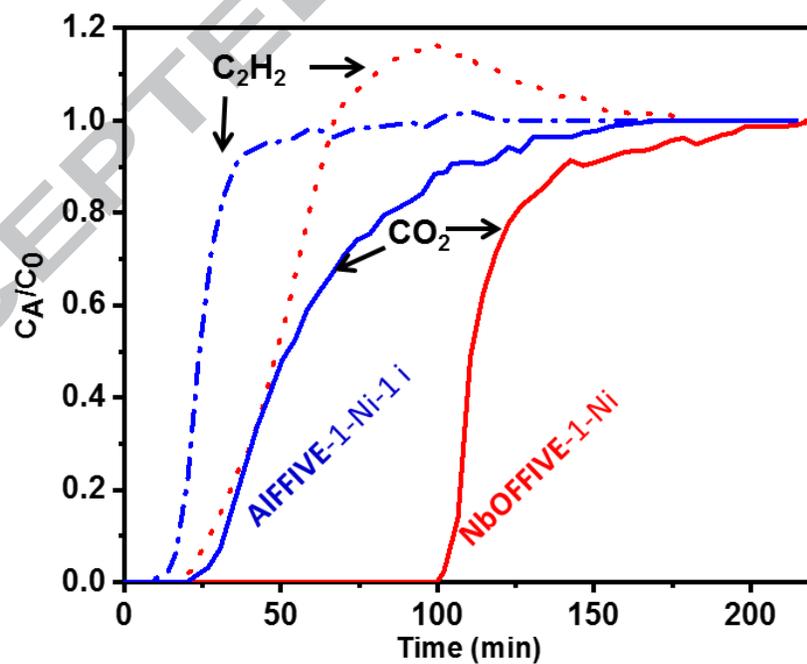


Figure 6. Column breakthrough tests **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** with CO₂/C₂H₂/He: 5/10/85 at 298 K and 1 bar total pressure (10 cm³/min flow rate).

Exploration of adsorptive separation of CO₂ from hydrocarbons in particular in the literature showed that classes of materials such as zeolites, carbon and MOFs do not show capability of selective removal of CO₂ from hydrocarbon in general and from C₂H₂ in particular. The introduction of the synergetic effect between thermodynamics and kinetics in case of this ultra-microporous fluorinated MOFs allowed to unveil the ideal environment for selective adsorption/desorption of CO₂. In light of the very close kinetic diameter between CO₂ and C₂H₂, we found it important to explore the effect of substituting the Al³⁺ and Nb⁵⁺ based organic pillars on the CO₂/C₂H₂ selective separation. Interestingly, as shown in figure 6, CO₂ is retained four times more than C₂H₂ in case of **NbOFFIVE-1-Ni** for test with CO₂/C₂H₂/He:5/10/85 mixture, while C₂H₂ is retained twice less in case of **AIFFIVE-1-Ni**. These results show that CO₂ is still dominating the selective adsorption when the pore environment is highly confined surrounding fluorines. The addition of potential open metal sites enhanced the interaction with C₂H₂ and reduced in turn the degree of pore confinement surrounding fluorines (The reason of such unusual CO₂ trapping is the interaction with the surrounding three fluorines (four fluorines in case of **NbOFFIVE-1-Ni** and three in case of **AIFFIVE-1-Ni**). This leads to favoring the C₂H₂ selective adsorption in case of **AIFFIVE-1-Ni**.

4. Conclusions

In this work, we unveiled for the first time the structure/separation properties relationships of two isostructural fluorinated MOFs, in particular the impact of the confined pore

environment together with the presence of coordinated or uncoordinated open metal sites for C₂H₂ adsorptive separation from C₂H₄ and CO₂. The substitution of [NbOF₅]²⁻ inorganic pillar by [AlF₅]²⁻ led to a reduction in the dominant CO₂ selectivity with more favorable affinity toward C₂H₂ at very low concentration. The ability of this platform to fine-tune the adsorption/separation property, driven by subtle structural differences, opens opportunities to enhance/control the performance of these materials as separation agents. Further work will focus on the selective separation of larger molecules like the separation C₄ olefins.

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Highlights

- Stable fluorinated Metal Organic Frameworks with tunable structural properties;
- Structural properties of **MFFIVE**-1-Ni with relation to C₂₊ adsorption were unveiled;
- Substitution of Nb⁵⁺ by Al³⁺ led to improved separation for C₂H₂/C₂H₄:1/99 system;
- **NbOFFIVE**-1-Ni shows unprecedented CO₂/C₂₊ selectivity in favor of CO₂;
- Substitution of Nb⁵⁺ by Al³⁺ affects the mechanism involved in C₂₊ separations;