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TOC

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CO₂ Capture Using The SIFSIX-2-Cu-i Metal-Organic Framework: A Computational Approach

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ABSTRACT

The adsorption of carbon dioxide and its separation from mixtures with methane using the recently synthesized **SIFSIX-2-Cu-i** metal-organic framework has been systematically studied by employing a variety of molecular simulation techniques. Quantum density functional theory calculations have been combined with force-field based Monte Carlo and molecular dynamics simulations in order to provide a deeper insight on the molecular-scale processes controlling the thermodynamic and dynamic adsorption selectivity of carbon dioxide over methane, giving particular emphasis on the mechanisms underlying the diffusion of the confined molecules in this porous hybrid material. The diffusion process was revealed to be mainly controlled by both (i) the residence dynamics around some specific interaction sites of the fluorinated metal-organic framework and (ii) the dynamics related to the process where faster molecules overtake slower ones in the narrow one-dimensional channel of **SIFSIX-2-Cu-i**. We further unveil a 1-dimensional diffusion behavior of both carbon dioxide and methane confined in this small pore MOF where single file diffusion is not observed.

I. Introduction

Natural gas processing is a relatively complex industrial process designed to refine raw natural gas by separating impurities and undesired hydrocarbons in order to meet several specifications, mainly related to its heat content and flame temperature.¹⁻⁷ Natural gas and biogas primarily consist of methane and to a lesser extent of carbon dioxide, hydrocarbons and hydrogen sulfide.¹⁻⁷ It was observed that the heat content of natural gas can be increased by reducing the amount of carbon dioxide.⁷ Therefore, the development of efficient methods to separate carbon dioxide from natural gas mixtures has become an issue of crucial importance over the last decade, in view also of the rapid decrease of fossil fuel resources.

The necessity to find efficient solutions to all these challenging issues regarding gas purification/storage has motivated a significant effort to develop novel types of porous materials as adsorbents in particular for the selective capture of carbon dioxide.⁸⁻²⁴ The key factor in the rational design of novel adsorbents is to tune their structural/chemical features to favor an equilibrium and/or kinetic separation or a full molecular sieving.²⁵⁻³² A very promising class of custom-designed inherently modular sorbents to achieve efficient gravimetric uptake and high CO₂ selectivity, combined with a low regeneration cost under practical conditions, is the class of metal-organic framework (MOF) materials.³³⁻³⁵ These materials are being developed by connecting metal-containing units (ions or clusters) with organic linkers in order to create open crystalline frameworks with permanent porosity. Due to the large variety of existing metal-containing building units and organic linkers, there is a wide range of candidate materials which can be designed for task-specific applications.³³⁻³⁵ However, the simultaneous tuning of the thermodynamic and kinetic selectivity, combined also with low energy costs related to the activation, regeneration and recycling of the sorbent material often poses daunting tasks to materials scientists.

In this context, some of us reported in a previous study²⁴ a crystal engineering strategy controlling the pore functionality and size in a series of metal-organic materials, by pillaring two-dimensional nets of organic ligands and metal nodes with hexafluorosilicate (SiF_6^{2-}) anions to form three-dimensional networks with primitive cubic (pcu) topology. The pore sizes within this family of materials, resembling pillared square grids, can be tuned by either changing the length of the organic linker and/or the metal node, or using the framework interpenetration approach. In this aforementioned study the synthesis of $[\text{Cu}(4,4'\text{-dipyridylacetylene})_2(\text{SiF}_6)]_n$, named as **SIFSIX-2-Cu**, was reported by performing the reaction of CuSiF_6 with 4,4'-dipyridylacetylene. The crystal structure of **SIFSIX-2-Cu** displays one-dimensional square channels with a pore dimension of 13.05 Å. It is also worthwhile to mention the report of an interpenetrated polymorph, named as **SIFSIX-2-Cu-i**, composed of double interpenetrated nets, which are isostructural to **SIFSIX-2-Cu**. The independent nets are staggered with respect to one another, significantly reducing the dimension of the one-dimensional square pore channels to 5.15 Å.

Adsorption measurements performed on both materials revealed that the CO_2 uptake of **SIFSIX-2-Cu-i** at ambient conditions and low pressure is relatively high as compared to other MOFs.³² Interestingly, the thermodynamic adsorption selectivity of CO_2 over CH_4 , estimated by the Ideal Adsorption Solution Theory (IAST) method applied to single component adsorption isotherms, is drastically enhanced in comparison with the non-interpenetrated **SIFSIX-2-Cu** framework.²⁴ This increase was assumed to be assigned to the stronger overlap of attractive potential fields of opposite walls in the relatively narrower pores of **SIFSIX-2-Cu-i**, leading to a high charge density and a higher CO_2 adsorption enthalpy.

However, in order to reveal deeper insights into the molecular-scale mechanisms controlling the thermodynamic and dynamic adsorption selectivity of carbon dioxide over methane in this material, a detailed description of the intermolecular interactions is required. The use of a

combination of quantum- and forcefield-based molecular simulations^{36,37} offers such a possibility. These techniques have been shown to have high predictive capabilities of macroscopic properties of complex materials such as MOFs.³⁸⁻⁴²

The main aim of the present study is to employ molecular modeling techniques in order to unravel the molecular-scale processes controlling the thermodynamic and dynamic adsorption selectivity of carbon dioxide over methane in **SIFSIX-2-Cu-i**, using advanced computational techniques ranging from quantum chemical calculations to atomistic forcefield based Molecular Dynamics and Monte Carlo simulation techniques. Particular emphasis was placed on the mechanisms underlying the diffusion of molecules in confined pores of the hybrid material using Molecular Dynamics, a strategy that we have intensively applied over the last decades to explore the diffusion of a series of gases in various MOFs.⁴³⁻⁵⁹

II. Computational Details

Cluster-based Density functional theory (DFT) calculations were first employed to determine the atomic charges of the two building blocks that form **SIFSIX-2-Cu-i**. The corresponding clusters cleaved from the experimental crystal structure taken from previous works²⁴, are presented in Figure 1. Single-point energy calculations were performed, keeping fixed the experimental geometry, using the PBE GGA functional⁶⁰ and the 6-31g(d,p) Gaussian basis set⁶¹ along the D3 dispersion correction introduced by Grimme *et al.*⁶² The atomic charges in each building block were estimated by employing the CHELPG scheme⁶³ to reproduce the molecular electrostatic potential at a number of points around the investigated molecular fragments of the MOF. All these calculations were performed using the Gaussian 09 software.⁶⁴

In order to build a force field for the atomistic molecular dynamics and Monte Carlo studies, the atomic charges obtained by the DFT calculations were used in combination with existing sigma and epsilon 12-6 Lennard-Jones (LJ) parameters taken from the literature. In particular,

the LJ parameters from the DREIDING⁶⁵ and the UFF⁶⁶ force fields were assigned to the atoms of the organic and inorganic building blocks of the MOF, respectively. The atomic charges corresponding to the 4,4'-dipyridylacetylene were taken from the calculation of the first building unit in Figure 1 and the charges for all the rest were extracted from the calculation of the second building unit. The experimental unit cell was then replicated 3 times along the x and y direction and 5 times along the z direction, creating in this way an almost cubic supercell, with x,y,z dimensions of 40.947, 40.947 and 40.460 Å, respectively. The supercell was saturated by adding terminal -NH₂ groups and the charges of the terminal atoms were adjusted in order to give a total zero charge to the supercell. The corresponding supercell is depicted in Figure 2. The charges and LJ parameters corresponding to each type of atoms in the MOF are summarized in Table 1.

Grand Canonical Monte Carlo (GCMC) simulations were performed at 303 K and in the pressure range of 0.05 - 1 bar in order to predict the binary mixture adsorption isotherms for CO₂ and CH₄ corresponding to an equimolar gas mixture. The GCMC simulations were carried out with the Complex Adsorption and Diffusion Simulation Suite (CADSS) code.⁶⁷ The rigid EPM2 and OPLS-AA force fields were employed for CO₂ and CH₄ molecules, respectively.^{68,69} These models provide very accurate descriptions of the structural, thermodynamic, transport and dynamic properties of CO₂ and CH₄, as well as of their mixtures, in a wide range of thermodynamic conditions.⁶⁸⁻⁷¹ Lorentz-Berthelot combining rules were employed for the LJ interactions between the different atoms of the adsorbate/adsorbent pairs. A cut-off of 12 Å was employed for short-range interactions while the Ewald summation method was considered for the electrostatic interactions. The fugacities for each adsorbed species at the investigated thermodynamic conditions were calculated using the Peng-Robinson equation of state.⁷² For each simulated state point, 2x10⁸ Monte Carlo steps were used for the equilibration and production runs, respectively. Several types of trial

molecular moves were taken into account: translation or rotation, creation or deletion and exchange of molecular identity.

After determining the amount of adsorbed CO₂ and CH₄ molecules in the framework corresponding to the equimolar mixture at 1 bar and 303 K, molecular dynamics (MD) simulations were performed in the canonical ensemble in order to investigate the mechanisms of diffusion of CO₂ in the pores of **SIFSIX-2-Cu-i** and related dynamics. The calculated average amount of adsorbed CO₂ and CH₄ molecules in the employed supercell corresponding to the bulk equimolar mixture at 1 bar and 303 K was 349 and 16 molecules, respectively. In the case of pure CO₂ the corresponding amount of adsorbed molecules was 410. However, to evaluate the impact of the presence of methane on the diffusion of CO₂, we performed MD simulation for pure confined CO₂ using a system consisting of 365 adsorbed CO₂ molecules, allowing the comparison of systems with exactly the same number of confined molecules.

In the case of the confined mixture, since the amount of adsorbed methane molecules is small and the arrangement of the molecules in the narrow one-dimensional pores could potentially affect the motional behavior of the molecules, 5 different MD simulations were performed for this thermodynamic state point, starting from different initial configurations. The initial configurations were produced by performing Monte Carlo simulations at the canonical ensemble, using 349 and 16 confined CO₂ and CH₄ molecules, as estimated by the GCMC simulations.

In order to investigate the temperature effects on the diffusion of the confined molecules and to calculate the related activation energy, MD simulations were performed in the canonical ensemble for the confined pure CO₂ at 350, 400 and 450 K using the same number of molecules. MD simulations at 400 and 500 K were also considered for the confined mixture containing 349 CO₂ and 16 CH₄ molecules. As in the case of 303 K, at each temperature five different simulations were performed for the confined mixture starting from different initial

conditions. The same force fields which were used in the GCMC simulations were also employed in the case of the MD simulations. The equations of motion were integrated using a leapfrog-type Verlet algorithm⁷³ and the integration time step was set to 1 fs. The intramolecular geometry of CO₂ and CH₄ molecules was constrained using the quaternion formalism.⁵⁶ A Nose-Hoover thermostat⁷⁴ with a temperature relaxation time of 0.2 ps was used to constrain the temperature during the simulations. All MD simulations were run for at least 20 ns using the DL_POLY simulation code.⁷⁵

III. Results and Discussion

The GCMC simulated adsorption isotherm of the bulk equimolar CO₂-CH₄ mixture at 303 K in **SIFSIX-2-Cu-I** is reported in Figure 3. The adsorption thermodynamic selectivity was further calculated by using the following equation:

$$S_{(CO_2/CH_4)} = \left(\frac{x_{CO_2}}{x_{CH_4}} \right) \cdot \left(\frac{y_{CH_4}}{y_{CO_2}} \right) \quad (1)$$

where x_i , y_i are the molar fractions of each component i ($i=CH_4$, CO₂) in the adsorbed and bulk phases, respectively.

The evolution of the selectivity of CO₂ over CH₄ as a function of pressure is also presented in Figure 3. The corresponding data confirm the preferential adsorption of CO₂ over CH₄ with a calculated selectivity at 1 bar and 303 K about 22 which is consistent with the previous value obtained by applying the IAST model from the single component adsorption isotherms²⁴. This so-obtained value is amongst the highest values reported so far for the best MOFs.³² The calculated adsorption enthalpies at low coverage for CO₂ and CH₄ of -40.7 and -28.3 kJ/mol, respectively confirm the very high affinity of the MOF framework to CO₂ consistent with the the previously reported experimental isosteric heat of adsorption for this gas molecule (-35 kJ/mol).²⁴ The preferential adsorption of CO₂ over CH₄ can also be evidenced by the shape

and intensities of the atom-atom radial distribution functions which have been calculated during the GCMC runs. Some representative radial distribution functions corresponding to the thermodynamically adsorbed binary mixture at 1 bar and 303 K are presented in figures S1-S3 in the Supporting Information. These radial distribution functions clearly confirm that the different adsorption sites of **SIFSIX-2-Cu-i** preferentially interact with CO₂ since the intensities of the main peaks, which are correlated with the strength of interactions, are higher than that corresponding to CH₄. This behaviour is consistent with the higher adsorption enthalpy calculated for CO₂.

The analysis of the trajectory obtained from the MD simulations of the adsorbed CO₂-CH₄ mixture at 1 bar and 303 K allowed us to extract the self-diffusion coefficients of CO₂ and CH₄ for the system containing 349 CO₂ and 16 CH₄ molecules using the well-known Einstein relation applied to the mean-square displacements for both guests averaged over all the MD trajectories and using a multi-time step origin.⁴³⁻⁵⁹ This led to D_s (CO₂) and D_s (CH₄) values of $0.88 \cdot 10^{-10}$ and $1.62 \cdot 10^{-10}$ m²/s, respectively, resulting in a self-diffusivity ratio of ~1.84 which can be related somehow to the kinetic selectivity of the MOF. Interestingly, the self-diffusivity for CO₂ is not lower than the value previously reported for other promising MOFs for CO₂ capture such as UiO-66(Zr)-(CO₂H)⁷⁶, ZIF-8⁷⁷ and MIL-91(Ti)^{11,78} and also for the reference zeolite NaX⁴⁸ for the same range of temperature. This observation suggests that kinetics is not expected to be a drawback for the use of **SIFSIX-2-Cu-i** in physisorption-based processes.

A further step consisted of exploring the diffusion mechanism of both molecules confined in **SIFSIX-2-Cu-i**. The Arrhenius plots dependence of the self-diffusion coefficient as a function of the inverse temperature are represented in Figure 5 for CO₂ in the adsorbed pure system and mixture. The corresponding activation energies for the pure system and mixture are 10.0 and 10.2 kJ/mol, respectively. The slightly higher activation energy corresponding to the

diffusion of CO₂ molecules in the mixture is consistent with the observation of a slightly lower self-diffusion coefficients in comparison with pure CO₂, signifying that the presence of CH₄ molecules tends to slow-down the dynamics of CO₂.

Previous studies revealed the strong interrelation between the self-diffusion of confined molecules and the residence dynamics related to the adsorbent-adsorbate interactions.^{79,80} These findings motivated us to further investigate the effect of these interactions on the self-diffusion of CO₂. In the first approach, since there are many interacting sites within **SIFSIX**-2-Cu-i MOF, the intermittent residence dynamics of CO₂ around the different interaction sites of the MOF was studied to determine the corresponding lifetimes. In this case the thermodynamically adsorbed CO₂ concentration at 303 K and 1 bar was used, containing 410 molecules in the **SIFSIX**-2-Cu-i supercell. The pair residence dynamics time correlation function for a couple of atoms i and j is defined as follows:

$$C_{res}(t) = \frac{\langle n_{ij}(0) \cdot n_{ij}(t) \rangle_{t^*}}{\langle n_{ij}(0)^2 \rangle} \quad (2)$$

where $n_{ij}(t)=1$ if a specific atom j is within a pre-defined cut-off distance of a second atom i at times 0 and t, and the atom j has only left the cut-off sphere for a period shorter than t^* during the time interval [0,t], otherwise $n_{ij}(t)=0$

The corresponding residence time is defined according to the following relation:

$$\tau_{res} = \int_0^{\infty} C_{res}(t) \cdot dt \quad (3)$$

According to this definition, $C_{res}(t)$ depends on the selection of the parameter t^* , and two limiting cases arise:

a) $t^*=0$, which corresponds to atom j remaining in the solvation cut-off sphere of atom i continuously for the whole time interval $[0, t]$. In this case we define the continuous residence time correlation function $C_{res}^C(t)$ and the corresponding continuous residence lifetime τ_{res}^C .

b) $t^*=\infty$, where the intermittent presence of atom j in the solvation cut-off sphere of atom i at time t is investigated, regardless of the number of exits and entrances of this atom into the cut-off sphere during the time interval $[0, t]$. In this case we define intermittent residence correlation function $C_{res}^I(t)$ and the corresponding intermittent residence lifetime τ_{res}^I .

In all these calculations a reference radial cut-off of 5.25 Å was used. This cut-off corresponds to the first minima of the RDFs for C(CO₂) - C₁ and C(CO₂) - C₂ and quite close to the second minimum of the RDF for C(CO₂) - F one (see Supporting Information). In general, since the shape of each calculated RDF is different, we decided to use the same reference cut-off distance criterion for all calculations. Additional tests using shorter and longer cut-off distances were also performed, revealing as expected that by increasing the cut-off distance the intermittent residence time correlation functions decay slower and the corresponding lifetimes increase. However, the general trends and conclusions are not affected by the cut-off criterion employed. The calculated intermittent residence lifetimes for the 5.25 Å cut-off are presented in Table 2. From this table it can be seen that the slowest dynamics correspond to the C (CO₂) - N and C (CO₂) - F interactions. This emphasizes that these MOF sites exhibit the more energetic interactions with the CO₂ molecules. To calculate the corresponding lifetimes, a sum of three exponential decay functions was used to model the time decay of the calculated intermittent correlation function. The calculated lifetimes are in the nanosecond range, reflecting in this way the relatively strong MOF/CO₂ interactions consistent with a self-diffusivity value in the range of 10⁻¹⁰ m²/s. In order to estimate the corresponding activation energies, the C (CO₂) - N intermittent residence dynamics were

investigated for the systems containing only 365 CO₂ molecules and in mixture made of 349 CO₂ and 16 CH₄ molecules at all the investigated temperatures. To illustrate the temperature dependence of these dynamics, the calculated C (CO₂) – N intermittent time correlation function corresponding to the pure CO₂ system is presented in Figure 5. The inverse temperature dependence of the logarithm of the average C (CO₂) – N intermittent residence lifetimes for the pure CO₂ system and the mixture is also presented in the same figure. The corresponding calculated activation energies for these residence dynamics, using again an Arrhenius equation, in the pure system and the mixture are 7.6 and 8.5 kJ/mol, respectively. The higher activation energy in the case of the mixture is consistent with the observation of a slower self-diffusivity for CO₂ in the mixture. At this point it has to be also noted that the ratio of the CO₂ diffusion coefficients in the pure system and the mixture is very similar to the inverse ratio of their corresponding C(CO₂) – N intermittent residence lifetimes. A similar behavior has also been reported in previous studies^{79,80}, further indicating the interrelation between adsorbent-adsorbate residence dynamics and the diffusion of the adsorbate molecules.

The fact that the calculated activation energies for the residence dynamics are lower than that corresponding to the diffusion process implies that the process where the adsorbed CO₂ molecules finally leave a specific region of the porosity of the MOF and move forward, is only one step of the diffusion mechanism. Understanding of the interactions between the adsorbate molecules themselves is also a key to provide a complete picture of the mechanisms related to the translational motions of the CO₂ molecules. Since **SIFSIX-2-Cu-i** is a material with very narrow pores and the CO₂ self-diffusion coefficient is relatively low, the existence or not of a single-file diffusion^{46,81-83} needs be further elucidated.

To that purpose, molecular by-passing effects and their related dynamics were studied in order to verify if faster CO₂ molecules can overcome their neighbour molecules in the one-

dimensional narrow pores. This by-passing mechanism for a pair of molecules with indices i, j is depicted in Figure 6 and the associated time correlation function has been defined as:

$$C_{Bypass}(t) = \frac{\langle h_{ij}(0) \cdot h_{ij}(t) \rangle}{\langle h_{ij}(0)^2 \rangle} \quad (4)$$

The calculation of this function was performed for specific CO₂-CO₂ pairs, taking into account the first neighbour j around each molecule i , which was identified at the time step $t=0$. The distance difference $z_{ij}(t) = z_j(t) - z_i(t)$ for these specific tagged pairs at $t=0$ was calculated for the whole time frame taken into account for the calculation of the time correlation function. In this way $h_{ij}(t)$ was estimated in the following way: if $z_{ij}(0) \cdot z_{ij}(t) > 0$ and this condition remains the same during the time interval $[0, t]$ then $h_{ij}(t) = 1$. However, the first time that $z_{ij}(0) \cdot z_{ij}(t) < 0$ then $h_{ij}(t) = 0$ and afterwards for all times $t' > t$ the corresponding value is $h_{ij}(t') = 0$. These cases are schematically represented in Figure 6 in order to provide a clear description of these dynamics. By definition, in the case of single-file diffusion it should always be $C_{Bypass}(t) = 1$. However, if the function starts to decay, this is a very clear indication of the absence of a single file diffusion. The calculated functions $C_{Bypass}(t)$ for the pure CO₂ system containing 365 molecules, but also for the mixture containing 349 CO₂ and 16 CH₄ molecules were calculated for all the investigated temperatures and they are presented in Figure 7. The decay of all the calculated functions verifies the absence of single file diffusion. However, the slow decay of $C_{Bypass}(t)$, especially at ambient temperature, also means that the dynamic process where CO₂ molecules overcome their closest neighbours is slow. The relaxation time of the function $C_{Bypass}(t)$ can provide very important information about these dynamic processes and the mechanisms controlling

the translation of the CO₂ in the narrow one-dimensional channels of **SIFSIX-2-Cu-i**. This relaxation time has been calculated using the equation:

$$\tau_{Bypass} = \int_0^{\infty} C_{Bypass}(t) \cdot dt \quad (5)$$

The temperature dependence of these relaxation times in the case of pure CO₂, but also for the mixture were investigated for CO₂-CO₂ pairs and the dependence of the logarithm of these relaxation times is presented in Figure 8. By using the Arrhenius equation the corresponding activation energies for this dynamic process were estimated to be 11.5 and 11.0 kJ/mol for the pure system and the mixture, respectively. The much higher activation energies in comparison with that obtained for the MOF-CO₂ residence dynamics indicate that from an energetic point of view it is more difficult for CO₂ molecules to overcome their neighbours in the narrow pore than to escape from a particular region of the pore where the molecules are preferentially interacting with adsorption sites. The fact that the activation energy related to the self-diffusion process is in between the activation energy values corresponding to the two different dynamic processes can be interpreted as a balance between these two different mechanisms affecting the translational behaviour of CO₂ molecules in the porosity.

It is also of interest to explore the structural alignment of CO₂ molecules in the channel of **SIFSIX-2-Cu-i**. To have a clearer picture, the distribution of the angles formed by the CO₂ molecular axis and the channel axis has been calculated and is presented in Figure 9. From the peaks of this distribution, it can be clearly seen that the CO₂ molecules can be distributed either parallel or perpendicular to the channel axis, with the parallel configurations being more preferable. This is supported by the shape of the calculated distributions corresponding to the pure CO₂ system with 365 confined molecules and the confined mixture with 349 CO₂ molecules and 16 CH₄ ones. As it also can be seen from Figure 9, the presence of CH₄

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2
3 molecules does not change the shape of the calculated distributions, which remain almost
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5 identical. A representative configuration, depicting the preferential parallel alignments of the
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7 CO₂ molecules in the channel of **SIFSIX-2-Cu-i** is presented in Figure 10.
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10 11 **IV. Conclusions** 12

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14 In the present article, a molecular simulation approach has been employed to study the
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16 adsorption of carbon dioxide and its separation from mixtures with methane using the recently
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18 synthesized **SIFSIX-2-Cu-i** metal-organic framework. We confirmed that **SIFSIX-2-Cu-i**
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20 exhibits a preferential adsorption of carbon dioxide over methane and the simulated
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22 thermodynamic selectivity at ambient conditions are in good agreement with the previously
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24 reported experimental value. Particular attention has been given to the investigation of the
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26 mechanisms underlying the diffusion of the confined molecules in the hybrid porous material,
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28 in order to provide a deeper insight into the molecular-scale processes controlling the
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30 thermodynamic and kinetic adsorption selectivity of carbon dioxide over methane in **SIFSIX-**
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32 **2-Cu-i**. The findings have revealed that the diffusion of CO₂ molecules in the narrow one-
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34 dimensional pores of **SIFSIX-2-Cu-i** is mainly controlled by the residence dynamics in the
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36 vicinity of some specific interaction sites of the MOF, particularly the nitrogen and fluorine
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38 atoms, and the dynamics related to the by-passing process where faster molecules overtake
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40 their slower neighbors in the channel. The higher activation energies for the by-passing
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42 dynamics in comparison with that obtained for the MOF-CO₂ residence dynamics indicate
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44 that from an energetic point of view the limit step for the diffusion of CO₂ is to overcome
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46 their neighbours in the narrow pore. The structural alignment of CO₂ molecules in the channel
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48 of **SIFSIX-2-Cu-i** has also been investigated, revealing that the CO₂ molecules are
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50 preferentially arranged parallel to the channel axis.
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Supporting Information Available

Representative atom-atom pair radial distribution functions corresponding to the thermodynamically adsorbed binary CO₂ – CH₄ mixture at 1 bar and 303 K are depicted in figures S1-S3.

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TABLES

Table 1: Partial charges and Lennard-Jones parameters corresponding to each type of atoms in the SIFSIX-2-Cu-i supercell. For the terminal nitrogen and hydrogen atoms the symbols NT and HT have been used, respectively. The different carbon types C₁-C₄ are depicted in Figure 1.

Interaction Site	q (e)	σ (Å)	ϵ (K)
Cu	0.700	3.2950	2.5178
Si	0.734	3.8264	202.2900
F	-0.370	3.0930	36.4830
N	-0.182	3.6621	38.9750

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NT	-0.69635	3.6621	38.9750
H	0.136	2.8464	7.6490
HT	0.276	2.8464	7.6490
C ₁	-0.226	3.4730	47.8570
C ₂	0.088	3.4730	47.8570
C ₃	-0.140	3.4730	47.8570
C ₄	0.300	3.4730	47.8570

Table 2: Calculated adsorbent-adsorbate intermittent residence lifetimes at 303 K for several atomic pairs in the system containing 410 adsorbed CO₂ molecules in the **SIFSIX-2-Cu-i** MOF.

Atomic Pairs	C (CO ₂) – C ₁	C (CO ₂) – C ₂	C (CO ₂) – C ₃	C (CO ₂) – C ₄	C (CO ₂) - N	C (CO ₂) - F
τ_{res}^I (ps)	4693	4649	2796	3955	5406	4777

FIGURES

Figure 1

Figure 2

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Figure 9

Figure 10

FIGURE CAPTIONS

Figure 1: The two building blocks of **SIFSIX-2-Cu-i** used for the DFT calculations. The colours corresponding to each atom are: Carbon (Grey), Hydrogen (White), Nitrogen (Blue), Fluorine (Light Blue), Silicon (Yellow) and Copper (Orange).

Figure 2: The **SIFSIX-2-Cu-i** supercell used for the MD and GCMC simulations. Atom colours are the same as in Figure 1.

Figure 3: Simulated adsorption isotherms for the co-adsorption CO_2/CH_4 corresponding to an equimolar bulk mixture at 303 K.

Figure 4: Arrhenius plot of the self-diffusion coefficient for CO_2 corresponding to the adsorbed pure CO_2 system containing 365 CO_2 molecules and adsorbed mixture containing 349 CO_2 and 16 CH_4 molecules.

Figure 5: Temperature dependence of the calculated C (CO_2) – N intermittent time correlation residence function $C_{res}^I(t)$ corresponding to the adsorbed pure CO_2 system containing 365 CO_2 molecules.

Figure 6: Schematic representation of the by-passing mechanism for a pair of molecules with indices i, j in the one-dimensional channel of **SIFSIX-2-Cu-i**.

Figure 7: Temperature dependence of the decay of the calculated function $C_{Bypass}(t)$, corresponding to the adsorbed pure CO_2 system containing 365 CO_2 molecules and adsorbed mixture containing 349 CO_2 and 16 CH_4 molecules.

Figure 8: Arrhenius plot of the average by-passing time τ_{Bypass} corresponding to CO_2 molecules and its nearest CO_2 closest neighbour at $t=0$, for the adsorbed pure CO_2 system containing 365 CO_2 molecules and adsorbed mixture containing 349 CO_2 and 16 CH_4 molecules.

Figure 9: Distribution of the angles formed by the CO_2 molecular axis and the one-dimensional channels axis of **SIFSIX-2-Cu-i** at 303 K, corresponding to the adsorbed pure CO_2 system containing 365 CO_2 molecules and the adsorbed mixture containing 349 CO_2 and 16 CH_4 molecules.

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Figure 10: A representative configuration from the MD simulations depicting the preferential parallel alignments of the CO₂ molecules in the one-dimensional pore channels of **SIFSIX-2-Cu-i**.

TOC graphics