

Molecular Simulation Study of CO₂ Removal from H₂ Stream by SIFSIX-3-Cu Adsorbent

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Abstract

The gradual depletion of fossil fuel reserves has renewed interest in hydrogen (H₂) as a durable and sustainable energy carrier. However, its successful application on an industrial scale hinges on removing trace contaminants particularly carbon dioxide (CO₂) from mixed gas streams. In this study, the separation of CO₂ from CO₂/H₂ mixtures was investigated using the metal organic framework SIFSIX 3 Cu and Grand Canonical Monte Carlo (GCMC) simulations across a wide range of temperatures and pressures. Two gas compositions (molar ratios CO₂/H₂ of 0.90/0.10 and 0.79/0.21) were examined between 298 K and 370 K. In every case, CO₂ uptake was markedly higher than that of H₂, and the adsorption of both gases decreased with increasing temperature. The Langmuir isotherm model provided an excellent fit to the observed data, indicating monolayer adsorption behavior. The isosteric heats of adsorption were calculated to be about 54 kJmol⁻¹ for CO₂ and roughly 2 kJmol⁻¹ for H₂, reflecting the stronger electrostatic attraction between CO₂ molecules and the SiF₆²⁻ sites in the framework. Spatial density distribution analysis revealed that CO₂ molecules preferentially occupy regions near the SiF₆²⁻ units, whereas H₂ molecules are mainly located around pyrazine rings. Overall, these findings highlight the pronounced CO₂ selectivity of SIFSIX 3 Cu even at low concentrations and underline its potential for hydrogen purification in industrial gas separation processes.

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1 Introduction

In view of the current energy crisis and the escalating environmental concerns associated with the substantial contribution of CO₂ to global warming and climate change, implementing effective strategies to manage and reduce CO₂ emissions has become imperative [1, 2]. Before the complete transition to renewable energy sources is realized, the development of technologies capable of efficiently capturing and storing CO₂ from fossil fuel based processes plays a crucial role in mitigating the carbon footprint. For this purpose, the use of clean and renewable energy sources to reduce dependence on fossil fuels is essential. Hydrogen (H₂), as a clean energy carrier with high energy density, non toxicity, renewability, and zero carbon emissions, has attracted significant scientific and industrial attention, positioning itself as one of the most promising candidates to replace conventional fossil fuels [3–6]. Nowadays, steam methane reforming (SMR) is widely used for hydrogen production in industrial processes. This process generates a mixture of gases, including hydrogen, water vapor, CO₂, CO, methane, and nitrogen, which must be purified before use [7]. One of the main operational challenges is the removal of CO₂ from gas streams, as even trace levels (up to 300 ppm) can impair the performance of alkaline fuel cells. Different methods and technologies have been developed to solve this problem. Aqueous amine solutions are commonly employed for post combustion CO₂ capture and can achieve high removal efficiency even at low concentrations [8]. However, amine processes have disadvantages including high energy requirements for regeneration, equipment corrosion, risks of amine leakage, high operating costs, and concerns about long-term storage stability [9]. Membrane based CO₂ separation is another possible approach, but suffers from the intrinsic trade off between permeability and selectivity for gases mixture [10]. The adsorption technique, which utilizes porous solid materials, has proven capable of outperforming other methods for capturing or separating CO₂ [6]. Advanced techniques such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) utilize solid adsorbents, notably zeolites and activated carbons [11]. Zeolites are crystalline aluminosilicates with microporous frameworks, noted for their high chemical and thermal stability. They require comparatively less energy for regeneration; however, their adsorption capacity is reduced under humid conditions due to competitive adsorption with water vapor [12]. Activated carbons are hydrophobic materials with large surface areas, offering high resistance to moisture. They perform effectively in gas separa-

tion under high pressure conditions; however, their efficiency can decline at lower pressures [13].

Performance of zeolites and activated carbons in CO₂ adsorption have investigated in numerous studies. Delgado et al. [14] showed that CO₂ has stronger electrostatic interactions with zeolite 13X and activated carbon. It is due to its quadrupole moment. Serafin et al. [15] synthesized activated carbons from fern leaves. Their results show that the sample prepared at 800 °C exhibited the highest CO₂ uptake (4.21 mmol/g at 45 bar). Krishna and van Baten [16] found that microporous zeolitic structures, such as NaY, have a high potential for selective CO₂ separation from gas mixtures, especially CO₂/H₂. Despite these advances, zeolites and activated carbons have limitations, especially at very low CO₂ concentrations. This limitation has attracted attention to new materials such as MOFs. MOFs are porous crystalline structures formed by the coordination of metal ions or clusters with organic linkers. Their high porosity, tunable pore size, chemical and thermal stability, and ability to be functionalized make them excellent candidates for CO₂ absorption, even at low concentrations [17, 18]. Mechanical and chemical stability is essential for the efficient and long term separation of CO₂. Nanostructuring enhances both mechanical strength and chemical resistance, enabling adsorbents to withstand high pressures, temperature fluctuations, and corrosive gases. Incorporating robust MOFs significantly improves structural integrity and helps maintain CO₂ adsorption capacity over extended periods [19, 20]. Nevertheless, the stability of MOFs under operating conditions remains a challenge; factors such as humidity, temperature variations, and the presence of other gases can lead to structural degradation or reduced selectivity [21, 22]. Commercial deployment requires a critical assessment of environmental impacts, scalability, life cycle performance, and reusability to ensure both environmental sustainability and economic feasibility [20]. In addition to mitigating CO₂ emissions, MOFs also play a role in hydrogen production by separating it from gases such as N₂ and CO in processes like steam methane reforming. Integrating renewable energy sources into these separation processes can substantially reduce environmental impact and strengthen the economic case for hydrogen as a clean fuel [23, 24].

Chernikova et al. [25] introduced a series of nanostructured MOFs known as SIFSIX-3-M (M = Cu, Ni, Zn), which demonstrate strong interactions and high selectivity toward CO₂ due to their narrow pore apertures and the presence of SiF₆²⁻ anions. Subsequent studies revealed that pore size and the position of fluorine atoms in SIFSIX-3-M structures play crucial roles in optimizing CO₂ adsorption [26–28]. Among these,

SIFSIX-3-Cu, with the smallest pore aperture, exhibited the highest adsorption energy and selectivity toward CO₂ over H₂.

In this study, for the first time, the adsorption performance of the advanced SIFSIX-3-Cu framework for selective separation of CO₂ from CO₂/H₂ mixtures with different compositions was systematically investigated using molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulations over a wide range of temperatures and pressures. The novelty of this research lies in the comprehensive analysis of the adsorption mechanism at the atomic level, focusing on spatial density distribution, preferred adsorption sites, and isosteric heat of adsorption – features that have rarely been addressed in such detail in previous studies. Furthermore, accurate modeling of CO₂ interactions with SiF₆^{2−} groups and prediction of adsorption behavior under practical operating conditions, particularly at low CO₂ concentrations, highlight the innovative aspect of this study. The findings provide a theoretical foundation for designing industrial gas separation processes with high efficiency and lower energy consumption.

2 Simulation Details

2.1 Simulation structures

This study was conducted using the Materials Studio software package. The three-dimensional structures of

the CO₂ and H₂ gas molecules, as well as the SIFSIX-3-Cu adsorbent, were constructed and imported based on the structural data reported by Shekhah et al. [29]. The atomic charges assigned to the CO₂ and H₂ molecules are summarized in Table 1, and the optimized structure of the SIFSIX-3-Cu framework with assigned charges is shown in Figure 1. The SIFSIX-3-Cu structure was then placed in a simulation box with dimensions of 23.7183 × 20.7558 × 20.7558 angstrom (Å) (Figure 2). The CO₂ molecule was modeled as a linear structure with a double bond between the carbon and oxygen atoms. All geometries were optimized using the built-in geometry optimization tools in the software to ensure the most energetically stable configurations. To simulate gas adsorption, CO₂ and H₂ were initially evaluated individually in their pure form within the SIFSIX-3-Cu framework. For hydrogen, simulations were performed over a temperature range of 298–370 K and a pressure range of 0.0001 to 200 kPa. For carbon dioxide, the same temperature range was used, while the pressure was varied from 0.0001 to 100 kPa. The resulting adsorption data were compared with the experimental results reported by Yuan et al. [30] at 298 K for validation purposes.

Table 1. Atomic charges of the adsorbate molecules [30]

Molecule	Atom	q/e
CO ₂	C	0.70
	O	−0.35
H ₂	H	0

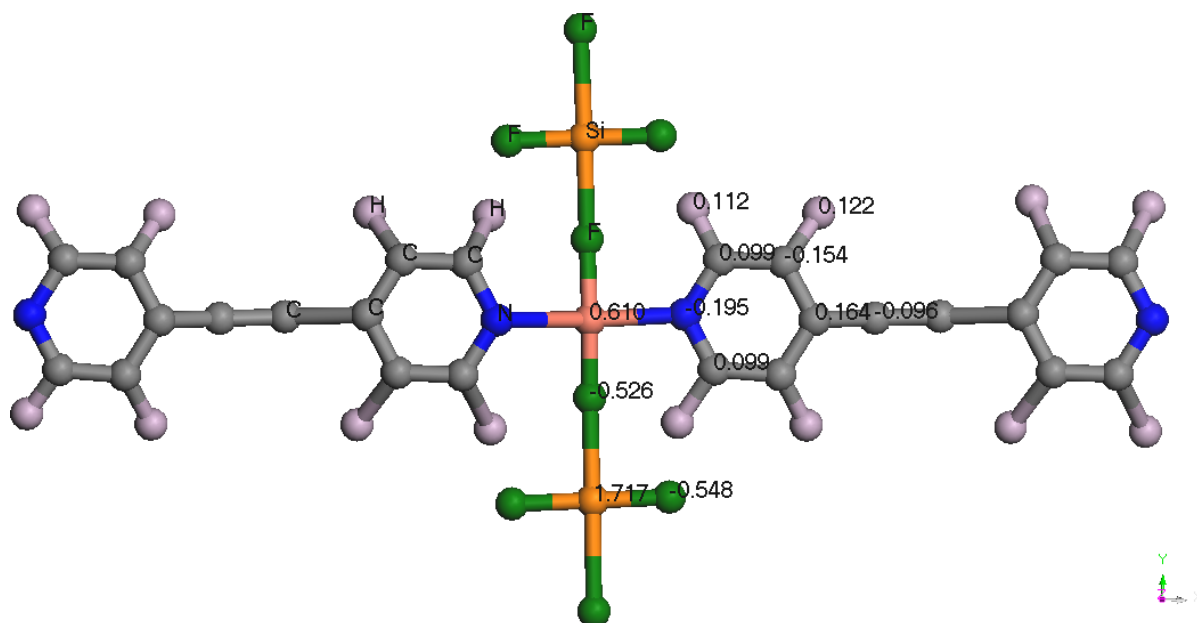


Fig. 1. Partial charges (e) for distinct atoms in SIFSIX-3-Cu

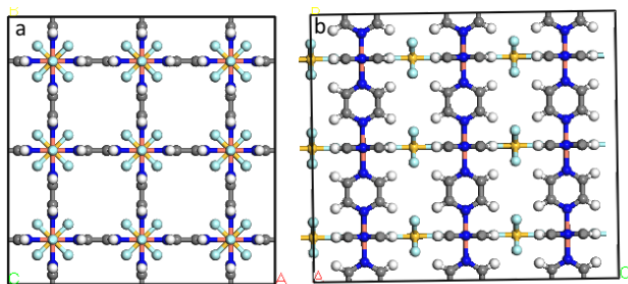


Fig. 2. Overall structure of the SIFSIX-3-Cu adsorbent from different views

2.2 Molecular simulation of adsorption

The adsorption behavior was modeled using Grand Canonical Monte Carlo (GCMC) simulations implemented in the Sorption module of Materials Studio. In the grand canonical ensemble, the system volume, temperature and chemical potential are held constant while the particle number fluctuates to represent exchange with an external gas reservoir [31]. Force fields and intermolecular potentials: Hydrogen molecules were represented using PCFF, whereas carbon dioxide and the SIFSIX 3 Cu framework were described with the Universal force field (UFF). Van der Waals interactions were treated with an atom based Lennard-Jones formalism and a spherical cutoff of 12.5 Å; long range electrostatic interactions were accounted for using Ewald summation beyond the cutoff.

The primitive SIFSIX 3 Cu unit cell was replicated into a $3 \times 3 \times 4$ supercell to reduce finite size effects. Periodic boundary conditions were applied in all three directions. At each state point (temperature and pressure condition) simulations comprised 1×10^6 Monte Carlo steps to secure equilibration prior to averaging thermodynamic observables.

2.3 Adsorption isotherm

Adsorption isotherm modeling is more important to understand and predict the adsorption behavior. In this study, the Langmuir isotherm model were used to analyze pure gas adsorption data. Langmuir isotherm is the simplest theoretical model assuming monolayer adsorption on a homogeneous surface. The Langmuir equation is defined as follows [32]:

$$\frac{q}{q_s} = \frac{kP}{1 + kP} \quad (1)$$

Here, k is the adsorption equilibrium constant, q_s is the maximum adsorption capacity, and P is the pressure. For multicomponent adsorption systems, the extended

Langmuir model was applied [32].

$$\frac{q_{e,i}}{q_{m,i}} = \frac{k_{sp,i} p_{e,i}}{1 + \sum_{i=1}^n k_{sp,i} p_{e,i}} \quad (2)$$

Here, $q_{e,i}$ is the equilibrium adsorption capacity of component i , $p_{e,i}$ is the equilibrium partial pressure of component i , $q_{m,i}$ is the maximum adsorption capacity of component i , and $k_{sp,i}$ is the isotherm constant for component i .

2.4 Adsorption selectivity

The selectivity of a component is a key parameter in evaluating adsorption-based separation performance with respect to a specific adsorbent. The following equation, denoted as Equation (3), is used to determine the adsorption selectivity [33]:

$$S_i = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} \quad (3)$$

The variables y_i and x_i represent the adsorbed amount and the molar fraction of CO_2 , respectively, while y_j and x_j correspond to the adsorbed amount and molar fraction of H_2 .

In this study, the following main assumptions were adopted: (1) the SIFSIX 3 Cu framework was treated as rigid, with no structural flexibility during adsorption; (2) the adsorption processes were assumed to be at equilibrium without chemical reactions between adsorbates and the framework; (3) periodic boundary conditions were applied in all directions; (4) long-range electrostatic interactions were treated with Ewald summation beyond the cutoff distance.

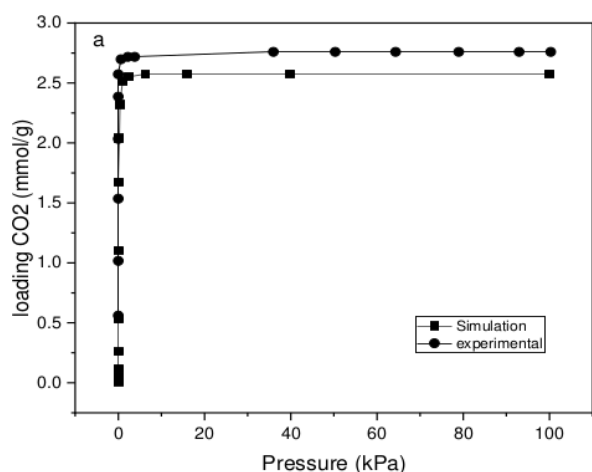
3 Results and Discussion

3.1 Validation of gas adsorption simulation for CO_2 and H_2 on SIFSIX-3-Cu

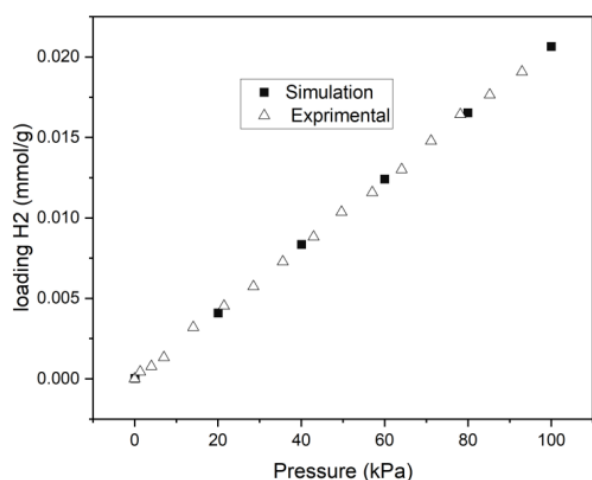
To evaluate the accuracy and reliability of the simulation procedure, the adsorption behavior of pure CO_2 and H_2 on the nanoporous adsorbent SIFSIX-3-Cu was simulated and analyzed at the standard temperature of 298 K. For validation purposes, the resulting adsorption isotherms were compared with the experimental and simulated data previously reported by Yuan et al. [30]. As illustrated in Figure 3, the simulation results obtained in this study exhibit a high degree of agreement with the reference data, particularly for CO_2 , indicating that the applied modeling approach is effective in reproducing the real behavior of the system.

It shows an acceptable agreement for hydrogen. Overall, the comparison confirms that the selected models and simulation parameters are sufficiently accurate and reliable. Therefore, these models can serve as a strong basis for further analysis over a wide range of temperature and pressure conditions.

Based on the comparison between simulated and experimental adsorption data for single-component gases on SIFSIX 3 Cu at 298 K, the average relative error (RE%) for H₂ was found to be approximately 3.35%, with individual errors ranging from 1.30% to 7.56%. For CO₂, the corresponding average RE% was about 3.03%, with values between 0.87% and 10.53%. These low error levels for both gases demonstrate the high accuracy of the simulation approach in reproducing experimental adsorption behavior.



(a)



(b)

Fig. 3. Comparison of pure (a) CO₂ and (b) H₂ adsorption isotherms on the SIFSIX-3-Cu adsorbent at 298 K, along with data reported by Yuan et al. [30].

3.2 CO₂ and H₂ adsorption isotherms at different temperatures

The adsorption of CO₂ and H₂ on SIFSIX-3-Cu was analyzed using the Langmuir isotherm. Adsorption simulations were conducted at 298, 310, 330, 350, and 370 K to investigate the effect of temperature on the adsorption process. The considered pressure range was from 0.001 to 100 kPa for CO₂ and from 10 to 200 kPa for H₂. It can enable a comprehensive evaluation of adsorption behavior under various operational conditions. The CO₂ adsorption isotherms are shown in Figure 4a, while the H₂ adsorption isotherms are presented in Figure 4b. The results obtained show that increasing temperature leads to a decrease in the adsorption capacity of both gases. This is consistent with the exothermic nature of the physical adsorption process. The highest adsorption capacity for both gases was observed at 298 K. In the CO₂ adsorption curve (Figure 4a), the steep slope of the isotherm at pressures below 20 kPa indicates a strong affinity of the adsorbent toward CO₂ in this region. Beyond this range, as pressure increases, the curve approaches saturation, and the adsorption capacity remains nearly constant, indicating the saturation of the adsorbent's active sites. The good fit of the data with the Langmuir model (Table 2) indicates that the adsorption process primarily occurs as a monolayer on uniform adsorption sites, which is a fundamental characteristic of this theoretical model. Examination of the isotherm parameters shows that the maximum adsorption capacity (q_s) for CO₂ is significantly higher than that for H₂, reflecting the high selectivity of the adsorbent structure toward CO₂. Furthermore, the decrease in both q_s and the adsorption equilibrium constant (K) with increasing temperature indicates the physical nature of the adsorption process and the influence of temperature in reducing the affinity of molecules for interaction with the adsorbent surface. Based on these observations, it can be concluded that SIFSIX-3-Cu possesses a high potential for effective CO₂ separation from gas mixtures at lower temperatures, and the Langmuir model serves as a reliable tool for predicting the adsorption behavior of this adsorbent.

3.3 Adsorption isotherms of CO₂/H₂ mixtures on SIFSIX-3-Cu

The results of pure CO₂ and H₂ demonstrated that the adsorption behavior of these gases follows the Langmuir isotherm model. Therefore, the adsorption isotherms of CO₂/H₂ gas mixtures at two different mole ratios (0.9/0.1 and 0.79/0.21) and in the temperature range of 298 to 350 K were also analyzed using extended langmuir model.

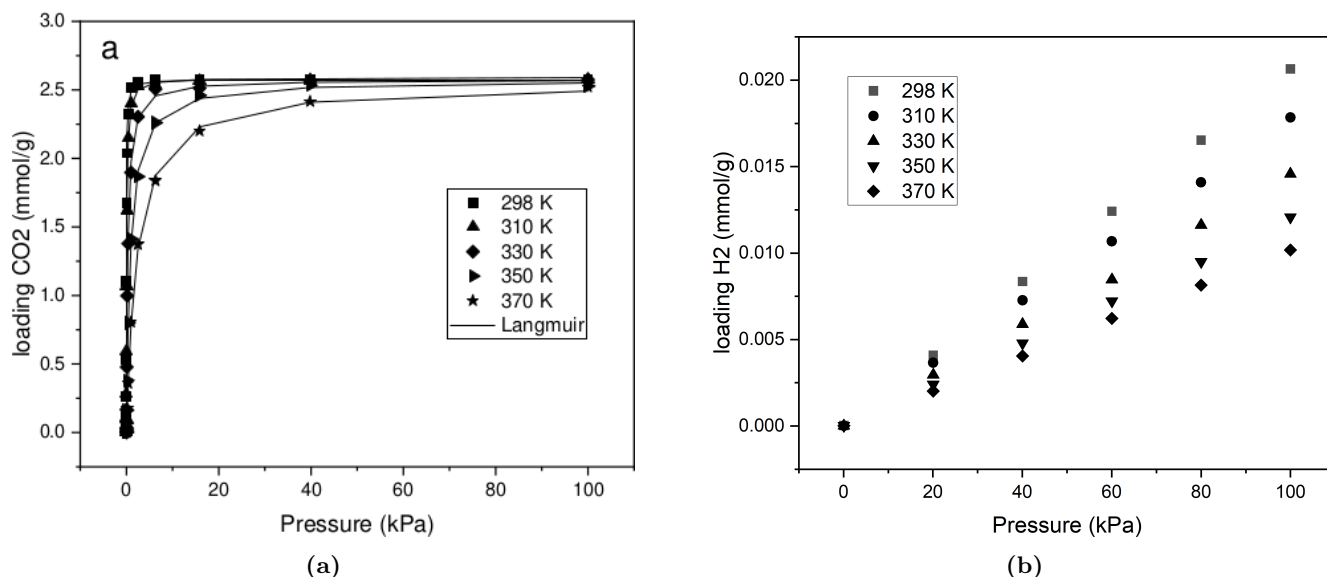


Fig. 4. Adsorption isotherms of pure CO₂ and H₂ on the SIFSIX-3-Cu adsorbent at temperatures of 298, 310, 330, 350 and 370 K: (a) CO₂ adsorption and (b) H₂ adsorption.

Table 2. Maximum adsorption capacity (q_s), adsorption constant (k), and coefficient of determination (R^2) in the Langmuir model for pure CO₂ and H₂

T K	H ₂			CO ₂		
	k	q_s	R^2	k	q_s	R^2
298	9.79E-05	2.12	0.9994	28.01	2.57	0.999
310	1.01E-04	1.65	0.999	11	2.59	0.999
330	8.1E-05	1.78	0.999	3.26	2.57	0.998
350	7.97E-05	1.51	0.999	1.14	2.57	0.999
370	7.28E-05	1.41	0.999	0.44	2.54	0.999

The simulated adsorption results for these mixtures are presented in Figure 5. The results show that the amount of CO₂ adsorbed was significantly higher than that of H₂, such that even at high hydrogen concentrations in the mixture, H₂ adsorption remained negligible. In contrast, CO₂ was adsorbed in considerable amounts, indicating the high selectivity of the SIFSIX-3-Cu adsorbent toward CO₂. This characteristic enables the efficient removal of CO₂ even at low concentrations, thereby facilitating the hydrogen purification process. Moreover, the results revealed that increasing temperature leads to a decrease in the adsorption capacity of both gases, which is consistent with the exothermic nature of physical adsorption. This behavior is attributed to the high polarity of the CO₂ molecule, enabling stronger interactions with the adsorbent sites and better dimensional compatibility with the porous structure of SIFSIX-3-Cu. In addition, the Langmuir model proves to be a reliable tool for de-

signing and predicting the performance of adsorption systems based on this material.

3.4 Adsorption selectivity in mixtures

The adsorption selectivity of the SIFSIX-3-Cu adsorbent for separating CO₂/H₂ binary mixtures was investigated through molecular simulations over a temperature range of 298 to 350 K. The results, presented in Figures 6 and 7, show that CO₂ selectivity is influenced by both gas concentration and temperature. Specifically, increasing the CO₂ concentration in the mixture leads to a decrease in selectivity. For instance, at a mole ratio of 0.79/0.21 (CO₂/H₂), lower selectivity was observed compared to the 0.9/0.1 ratio. Furthermore, an inverse relationship was found between temperature and selectivity, with the highest selectivity recorded at 298 K, the lowest temperature studied. Figure 6 illustrates the CO₂/H₂ adsorption selectivity behavior at a mole ratio of 0.9/0.1 within the SIFSIX-3-Cu framework. Figure 6a presents results at 298, 310, and 320 K, while Figure 6b shows data at 330, 340, and 350 K. Similarly, Figure 7 displays the selectivity behavior for the 0.79/0.21 mixture across the same temperature intervals. These findings highlight the excellent performance of SIFSIX-3-Cu as an efficient adsorbent for CO₂ separation from hydrogen-containing gas streams, particularly under conditions of low CO₂ concentration and lower temperature. This property enhances its potential for practical applications in hydrogen purification processes.

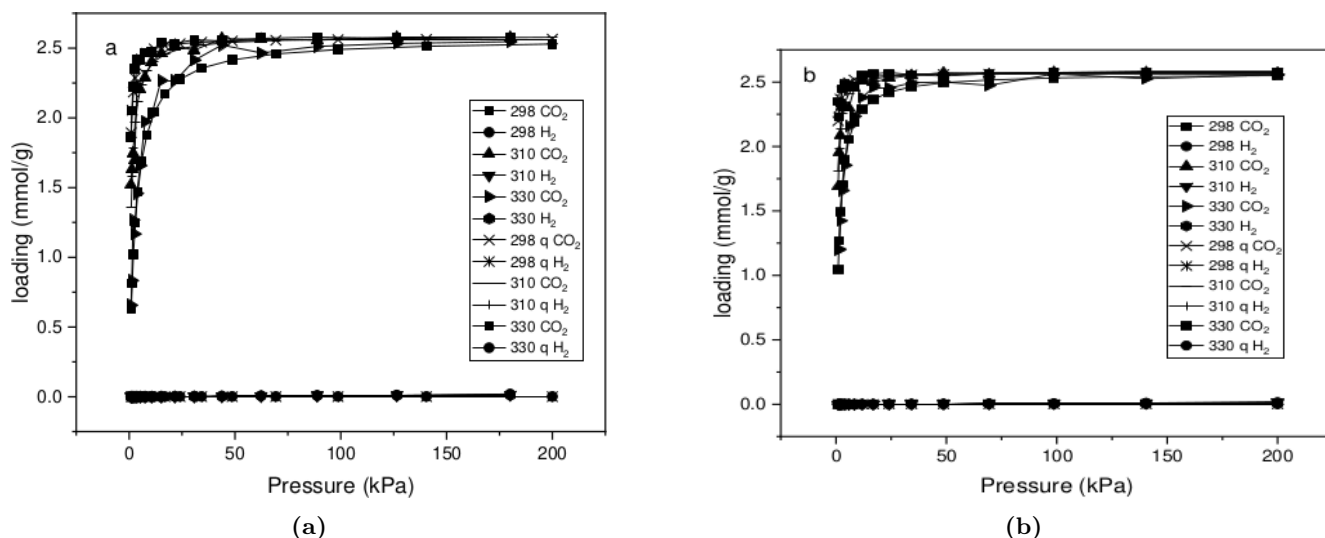


Fig. 5. Simulated adsorption isotherms of CO₂/H₂ binary mixtures on SIFSIX-3-Cu at different temperatures (298–350 K), based on the Langmuir model: (a) mole ratio 0.9/0.1 and (b) mole ratio 0.79/0.21.

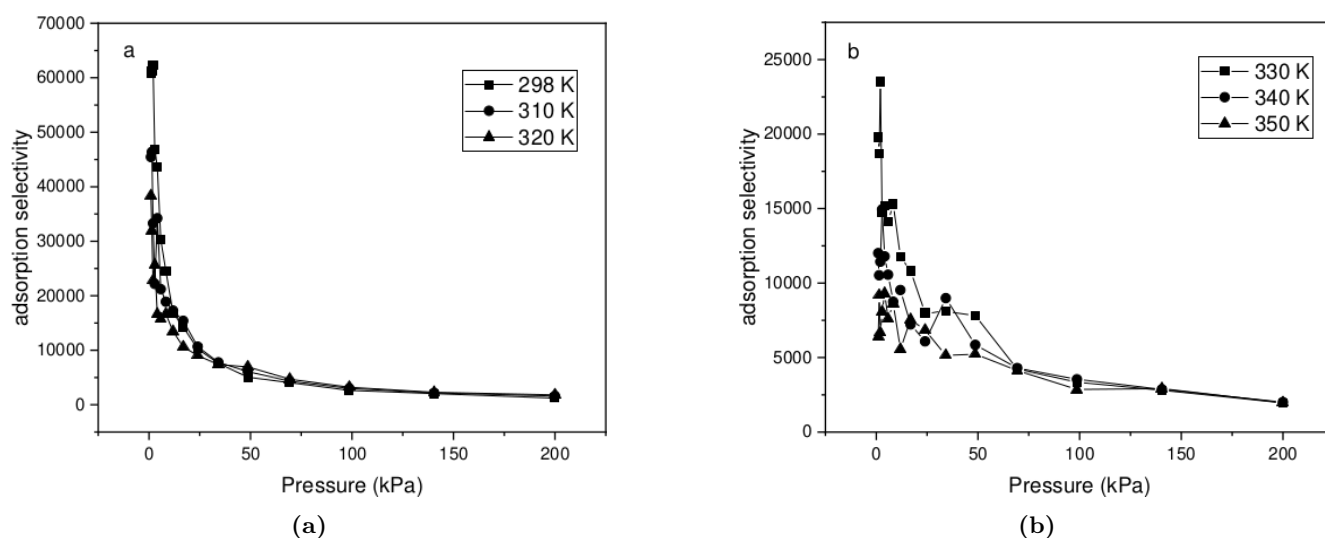


Fig. 6. Adsorption selectivity of CO₂/H₂ mixture with a mole ratio of 0.9/0.1 on SIFSIX-3-Cu: (a) at 310, and 320 K, and (b) 330, 340, and 350 K.

3.5 Spatial density distribution of CO₂ and H₂ in the SIFSIX-3-Cu framework

To investigate the preferred adsorption sites of CO₂ and H₂ molecules within the SIFSIX-3-Cu structure, molecular dynamics simulations were conducted at 298 K using a $3 \times 3 \times 3$ supercell. This approach eliminates boundary effects and accurately represents the periodic behavior of the framework. The spatial density distribution results reveal that H₂ molecules primarily concentrate at the center of the pyrazine

rings, indicating preferential and relatively strong interactions between H₂ and the aromatic regions of the framework (Figure 8). In contrast, the adsorption sites for CO₂ exhibit a more ordered arrangement and are mainly located within a distinct plane composed of SiF₆²⁻ anions, commonly referred to as the “silicon plane” (Figure 9). This behavior is driven by electrostatic interactions: attractive forces between the electropositive carbon atom in CO₂ and the electronegative fluorine atoms in the framework, and repulsive forces between the electronegative oxygen atoms

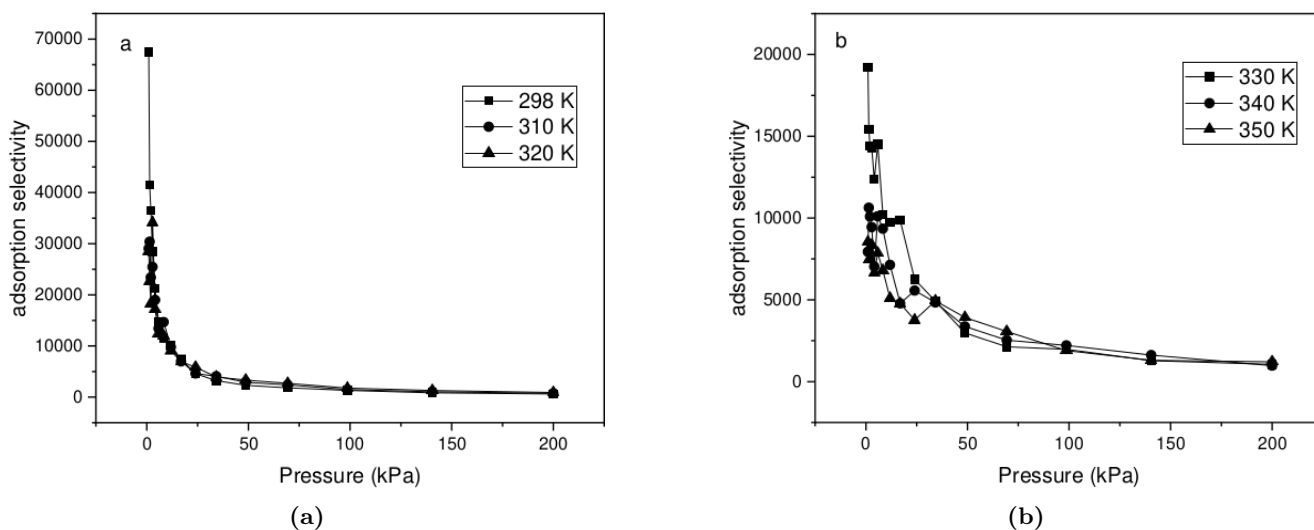


Fig. 7. Adsorption selectivity of CO₂/H₂ mixture with a mole ratio of 0.79/0.21 on SIFSIX-3-Cu: (a) 310, and 320 K, and (b) 330, 340, and 350 K.

of CO₂ and those same fluorine atoms. Consequently, CO₂ molecules tend to stabilize at the center of four equatorial fluorine atoms. These findings, further confirmed by the data in Figure 10, demonstrate that SiF₆²⁻ anions play a key role in the selective interaction with CO₂, while their effect on H₂ adsorption is negligible. Overall, these results highlight that the unique structure of SIFSIX-3-Cu creates specific adsorption sites and stronger interactions for CO₂, making it an excellent candidate for targeted gas separation and purification applications, particularly for CO₂. These insights may serve as a theoretical foundation for the rational design of advanced MOF adsorbents.

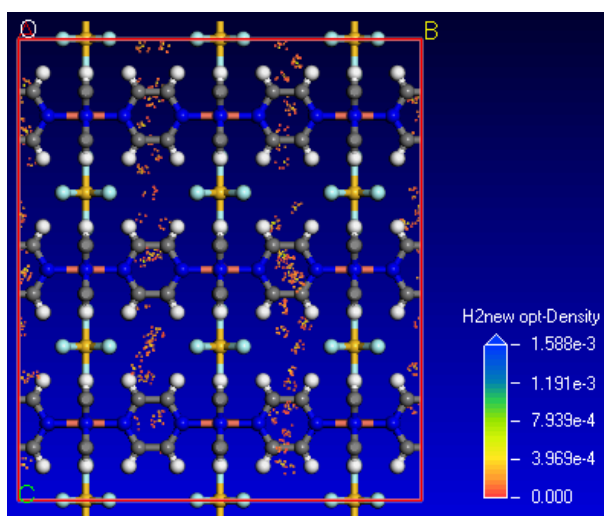


Fig. 8. Spatial density distribution of H₂ in SIFSIX-3-Cu at 298 K, shown from front and top views. Atom color scheme: F = turquoise, Cu = copper, Si = yellow, H = white, C = gray, N = blue.

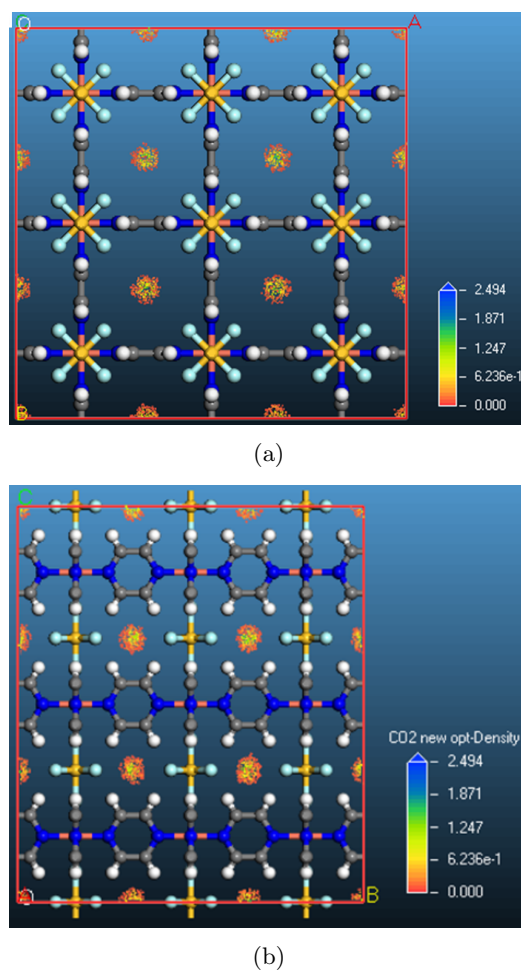


Fig. 9. Density centers of CO₂ in SIFSIX-3-Cu at 298 K: (a) front view, (b) top view. Atom color scheme: F = turquoise, Cu = copper, Si = yellow, H = white, C = gray, N = blue.

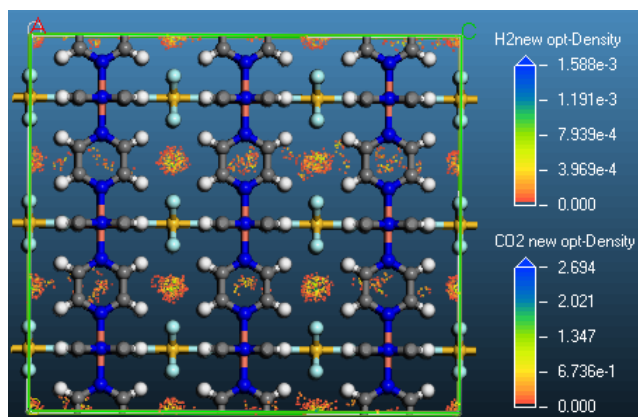


Fig. 10. Density centers of CO₂ and H₂ in SIFSIX-3-Cu at 298 K: (a) front view, (b) top view. Atom color scheme: F = turquoise, Cu = copper, Si = yellow, H = white, C = gray, N = blue.

3.6 Isotheric heat of adsorption (Q_{st}) of CO₂ and H₂

The isotheric heat of adsorption (Q_{st}) reflects the strength of interactions between the adsorbent framework atoms and the adsorbate molecules. Q_{st} for gases in porous materials is calculated based on adsorption isotherms measured at different temperatures. Accordingly, the isotheric heat of adsorption was determined from the adsorption isotherms measured at 298, 310, 330, 350, and 370 K. For SIFSIX-3-Cu, the isotheric heat of adsorption for CO₂ reaches approximately 54 kJ/mol at relatively low pressures (Figure 11). This high value is attributed to the ability of CO₂ molecules to form one-dimensional chains through strong binding interactions between electronegative F[−] ions and the electropositive carbon atom of CO₂ [34]. SIFSIX-3-Cu possesses ultra-micropores whose sizes can be tuned by exchanging organic ligands and metal ions within the framework, thereby ensuring a high affinity for CO₂. Importantly, the Q_{st} values remain nearly constant over the selective adsorption range of CO₂ (Figure 11), indicating the presence of a single type of adsorption site. The high CO₂ adsorption capacity of the MOF can be mainly attributed to the small pore size (~ 0.32 nm), which is even smaller than the kinetic diameter of the CO₂ molecule (~ 0.33 nm) [22]. The adsorption of CO₂ is significantly influenced by electrostatic interactions within the framework channels due to the molecule's quadrupole moment, as illustrated in Figure 11. Regarding the isotheric heat of adsorption, the trend shows an initial increase due to the availability of vacant adsorption sites, followed by a slight decrease, and then stabilizes at a constant value, indicating pore saturation. Interestingly, once the ad-

sorption capacity reaches saturation and pressure continues to rise, Q_{st} fluctuates around a constant value, suggesting that the filled pores likely reduce further CO₂ adsorption capacity. There is a direct relationship between isotheric heat of adsorption and selectivity; higher Q_{st} values correspond to higher adsorption selectivity. Therefore, the highest selectivity for CO₂ adsorption is observed at 298 K.

In contrast, the H₂ adsorption curve is linear with a nearly constant and low isotheric heat of adsorption, shown in Figure 12. In this study, the isotheric heat of adsorption for H₂ is approximately 2 kJ/mol, indicating a very low affinity of SIFSIX-3-Cu for hydrogen. This highlights its excellent potential for removing impurities such as CO₂ from hydrogen streams.

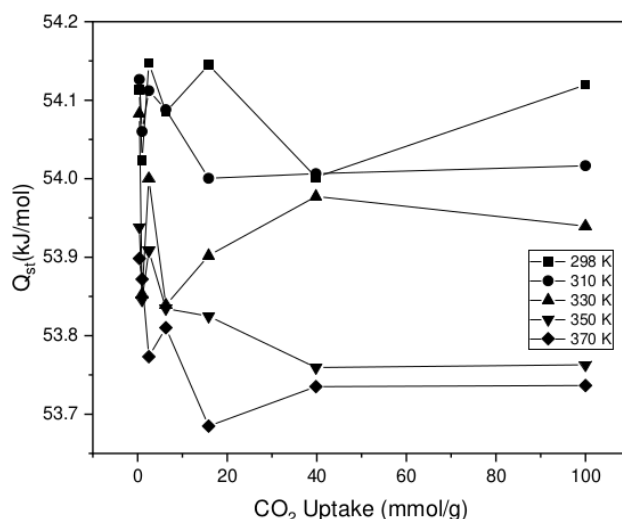


Fig. 11. Isotheric heat of adsorption (Q_{st}) for CO₂ at 298 K as a function of loading in SIFSIX-3-Cu.

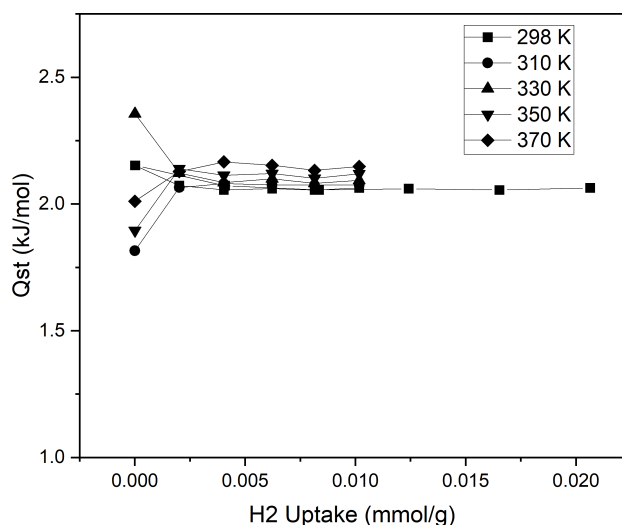


Fig. 12. Isotheric heat of adsorption (Q_{st}) for H₂ at 298 K as a function of loading in SIFSIX-3-Cu.

Figure 13 compares the CO₂ adsorption performance of SIFSIX 3 Cu obtained in the present study with literature data for MIL 101, USTA 16, and ZIF 8 over a similar pressure range. While USTA 16 exhibits a larger maximum uptake at higher CO₂ pressures, SIFSIX 3 Cu clearly outperforms all other adsorbents in the low pressure region (< 20 kPa), which is particularly relevant for the removal of trace CO₂ from hydrogen streams. This superior performance at low pressures is attributed to the strong electrostatic interactions between CO₂ molecules and the SiF₆²⁻ anions within the ultra microporous framework. In contrast, MIL 101 and ZIF 8 show considerably lower adsorption capacities throughout the entire pressure range, underscoring the exceptional suitability of SIFSIX 3 Cu for trace level CO₂ capture in hydrogen purification processes.

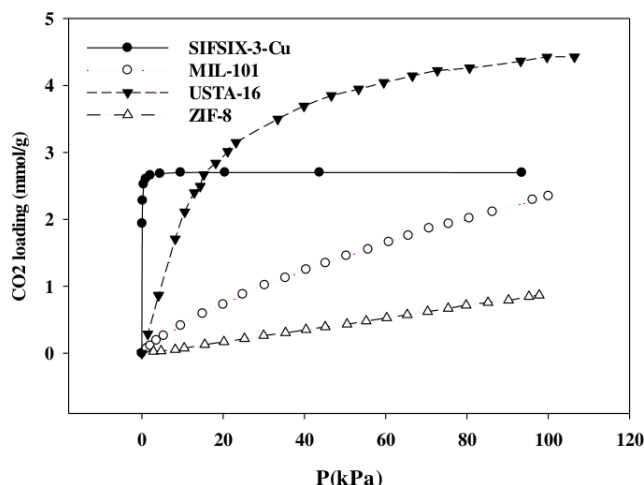


Fig. 13. Comparison of CO₂ adsorption isotherms at 298 K for SIFSIX 3 Cu (this work) and previously reported data for MIL 101 [35], USTA 16 [36], and ZIF 8 [37]

3.7 Limitations and drawbacks

In practical industrial hydrogen production processes, such as steam methane reforming (SMR), the effluent gas stream exiting the reformer typically contains significant amounts of water vapor along with CO₂, H₂, and other minor components. While the exceptional CO₂ selectivity and capacity of SIFSIX 3 Cu make it a promising candidate for hydrogen purification, it is well established in the literature that the structural stability of many MOFs, including fluorinated ultramicroporous frameworks, can be adversely affected by prolonged exposure to moisture or liquid water. Hydrolytic degradation may lead to partial loss of crystallinity, reduced pore volume, and diminished adsorption capacity over repeated cycles. Therefore, to ensure reliable long term

operation, it is necessary to remove water vapor prior to feeding the gas into the MOF adsorption bed. This can be readily achieved by placing a hydrophilic desiccant bed (e.g., silica gel, activated alumina, or zeolitic 3A/4A materials) upstream of the MOF column to dry the gas stream to an acceptable dew point. Such pre drying units are mature and widely implemented in gas processing plants, and their integration into the process flow has negligible impact on overall system complexity or cost. Since the separation process described in this study is conducted at near ambient temperatures, thermal stability is not a critical limitation for SIFSIX 3 Cu under these conditions. By combining conventional dehydration technology with the high selectivity SIFSIX 3 Cu adsorption stage, the detrimental effects of humidity on MOF stability can be effectively mitigated, enabling sustained structural integrity and adsorption performance over extended operational periods, even under industrially relevant conditions.

Although the present study focuses on evaluating the adsorption performance of SIFSIX 3 Cu at the molecular scale, a comprehensive economic and energy consumption analysis would require detailed process design, including the sizing of adsorption columns and regeneration units. Such engineering design and associated techno economic assessments are beyond the current scope but are planned for future research to evaluate the large scale feasibility of this adsorption process.

4 Conclusion

This study investigated the performance of the SIFSIX-3-Cu adsorbent for CO₂/H₂ gas mixture separation using GCMC simulation. The results demonstrated a significantly higher selectivity of SIFSIX-3-Cu toward CO₂, even in the presence of high H₂ concentrations. The highest CO₂ uptake was observed at 298 K and 15 kPa, reaching 2.58 mmol/g, whereas the H₂ uptake remained low at only 0.14 mmol/g. This behavior is attributed to strong electrostatic interactions between the fluorine atoms in the framework and the quadrupole moment of CO₂. An increase in temperature led to a decrease in adsorption capacity, consistent with the exothermic nature of physical adsorption. Additionally, the adsorbent's selectivity improved with decreasing CO₂ concentration in the mixture, showing the highest selectivity at a CO₂/H₂ molar ratio of 0.9/0.1. Spatial density distribution analysis confirmed that CO₂ molecules preferentially adsorb near SiF₆²⁻ anions, while H₂ tends to accumulate at the center of pyrazine rings. The isosteric heat of adsorption (Q_{st}) values further confirmed the stronger interaction of CO₂ with the adsorbent compared to H₂ (approx-

mately 54 kJ/mol vs. 2 kJ/mol). These findings suggest that SIFSIX-3-Cu is an excellent candidate for industrial applications such as hydrogen purification and CO₂ capture from gas streams, especially under low-temperature and moderate-pressure conditions. For future work, it is recommended to investigate the effect of water vapor and other impurities on the adsorbent's performance.

Declaration of Generative AI and AI-assisted technologies in the writing process During the preparation of this manuscript, the authors made use of AI tools (for translation assistance and grammar refinement) to enhance the English writing quality and overall readability of the text. All outputs generated by these tools were carefully reviewed and edited by the authors, who take full responsibility for the content of this publication.

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