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Research Article

Comparative Study of Selective CO_2 Adsorption in the Presence of Moisture by UiO-66 and MIL-53(Al) Metal-Organic Frameworks Using Molecular Dynamics Simulation

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ABSTRACT

This study presents a comparative molecular dynamics investigation of the CO_2 capture performance of the hydrostable UiO-66 and the flexible MIL-53(Al) metal-organic frameworks under humid flue gas conditions, focusing on dynamic competition and kinetic behavior. Simulations across a wide range of relative humidity (0-100% RH) at 313 K reveal that UiO-66 achieves superior and stable performance, characterized by a high CO_2 /H_2O selectivity of 12.5 ± 1.1 at 50% RH, which is more than three times that of MIL-53(Al) (3.8 ± 0.5). This advantage is fundamentally attributed to UiO-66's exceptional structural stability, which prevents framework degradation and preserves active adsorption sites in the presence of water. In contrast, MIL-53(Al) undergoes a pronounced breathing transition above 75% RH, leading to a ~35% unit cell volume collapse and a drastic reduction in CO_2 uptake capacity. Kinetic analysis further demonstrates the operational superiority of UiO-66, which reaches 90% of its equilibrium CO_2 capacity within 12 ± 2 minutes, compared to over 35 ± 5 minutes for MIL-53(Al). This rapid kinetics is supported by a CO_2 self-diffusivity in UiO-66 ($(2.1 \pm 0.3) \times 10^{-9}$ m²/s) that is nearly five times higher than in MIL-53(Al). The results unequivocally identify structural hydrostability as the critical parameter for effective CO_2 capture in humid environments, establishing UiO-66 as a highly promising and robust candidate for post-combustion carbon capture technologies.

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Introduction

The escalating concentration of atmospheric carbon dioxide (CO_2) has been identified as a primary driver of global climate change, necessitating urgent and effective mitigation strategies [1]. According to the Intergovernmental Panel on Climate Change (IPCC), a substantial fraction of anthropogenic CO_2 emissions originates from industrial point sources

such as thermal power plants, cement factories, and refineries [2]. In this context, post-combustion capture (PCC) technologies have emerged as a vital and immediate approach for reducing greenhouse gas emissions from these flue gas streams [3].

A critical and often debilitating challenge in practical PCC implementation is the ubiquitous presence of water vapor. Industrial flue gases are inherently humid, and water molecules, being highly polar, compete aggressively with CO_2 for adsorption sites within porous materials. This competitive adsorption can drastically reduce both the capacity and selectivity of the adsorbent, undermining the overall efficiency of the capture process [4, 5]. Consequently, the development of adsorbents that combine high CO_2 affinity with exceptional stability under humid conditions is paramount for advancing PCC technologies towards industrial reality [6].

The evolution of porous adsorbents has seen significant progress from early coordination polymers and supramolecular metal-organic systems to the highly engineered architectures of modern metal-organic frameworks (MOFs). Pioneering work on coordination polymers laid the conceptual foundation for tunable porosity and functionality, with studies on sonochemical synthesis and morphology control demonstrating the profound impact of synthetic pathways on final structure and properties [7-9]. These systems highlighted the critical relationship between metal-ligand coordination strength, network connectivity, and the resulting material's stability principles that directly inform the design of robust MOFs.

In recent years, MOFs have risen to the forefront of materials research for gas separation due to their extraordinary properties, including record-high surface areas, tunable pore geometries, structural diversity, and synthetic tailorability [10]. Building upon the foundational concepts from coordination chemistry, zirconium-based UiO-66 and aluminum-based MIL-53(Al) have shown particular promise for selective CO_2 capture [11]. UiO-66,

first reported by Cavka et al. in 2008, has rapidly established itself as a benchmark material in gas adsorption studies, renowned for its exceptional chemical and hydrothermal stability a trait attributed to its strong Zr_6 O_4 $(OH)_4$ secondary building units [12]. In contrast, MIL-53(Al) exhibits a fascinating "breathing" behavior, whereby its crystal structure reversibly changes pore volume in response to guest molecules like CO_2 or H_2 O [13]. This flexibility, while mechanistically interesting, introduces a complex dependency on operating conditions that can compromise performance in humid environments.

Although the adsorption properties of UiO-66 and MIL-53(Al) have been extensively studied individually, a systematic, molecular-level comparison of their performance under a comprehensive range of relative humidity (0-100% RH), simulating real flue gas conditions, remains less explored. Prior computational and experimental studies have often focused on dry conditions or limited humidity ranges. This study aims to fill this gap by providing new mechanistic insights into the interplay between framework hydrostability, competitive adsorption, and diffusion kinetics under realistic humid conditions. Molecular dynamics (MD) simulation serves as a powerful tool for this investigation, enabling the atomic-scale probing of molecular interactions, adsorption site competition, and transport phenomena [14]. While MD is excellent for studying diffusion, kinetics, and dynamic structural responses, we acknowledge that for predicting precise adsorption isotherms, particularly at high loadings, Grand Canonical Monte Carlo (GCMC) simulations are often the method of choice. This MD study complements such thermodynamic approaches by focusing on the dynamic and kinetic behavior that governs performance in flowing, humid systems. This approach not only allows for the prediction of performance metrics like selectivity but also provides fundamental insights into the structural integrity and adsorption kinetics of MOFs under operational stressors [15].

The primary hypothesis of this work is that the inherent hydrostructural stability of a MOF, rather than its adsorption capacity under ideal conditions, is the decisive factor governing its CO_2 capture performance in humid flue gas. We specifically hypothesize that: (i) UiO-66 will maintain superior and stable CO_2 /H_2 O selectivity across the humidity range due to its rigid framework, and (ii) the breathing transition of MIL-53(Al) at high RH will lead to a catastrophic loss in CO_2 capacity and diffusivity, despite its potential under dry conditions.

Accordingly, this research employs molecular dynamics simulations to conduct a comparative investigation of UiO-66 and MIL-53(Al) for simultaneous CO_2 and H_2 O adsorption under simulated flue gas conditions. The main objectives are: (1) to determine the CO_2 and H_2 O adsorption isotherms across a 0-100% RH range at 313 K, (2) to calculate the CO_2 /H_2 O selectivity as a function of humidity, (3) to analyze the adsorption kinetics and diffusion coefficients of both gases, and (4) to correlate the observed performance directly with the structural stability or dynamics of each framework in the presence of moisture.[16.17]. The following sections are structured as follows: Section 2 details the computational methodology, including crystal structure modeling, force field selection, and simulation protocols. Section 3 presents and discusses the results on adsorption equilibrium, selectivity, kinetics, and structural behavior. Finally, Section 4 summarizes the key conclusions and their implications for the selection and design of MOFs for industrial carbon capture.

2. Materials and Methods

2.1. Crystal Structure Modeling

The initial crystal structures of UiO-66 and MIL-53(Al) were obtained from the Cambridge Structural Database (CSD) [10]. To ensure statistical significance and minimize periodic

boundary effects, the primitive unit cells were expanded to create supercells with minimum dimensions of 3×3×3. This specific size was selected based on convergence tests to balance computational cost with accuracy. Prior to the molecular dynamics (MD) simulations, all expanded structures underwent a geometric energy minimization process using the conjugate gradient algorithm. This optimization was performed until the force on each atom was reduced below a threshold of 10^{-4} eV/Å, ensuring a stable and relaxed starting configuration for subsequent simulations. The following force fields and molecular models were employed to describe the interatomic interactions.The Universal Force Field (UFF) [5] was used to model the intra-framework interactions within both UiO-66 and MIL-53(Al). The UFF was selected for its proven transferability across the periodic table and its demonstrated reliability in modeling structural properties and guest-framework interactions in diverse MOF topologies, including zirconium- and aluminum-based systems, providing a balanced compromise between accuracy and computational efficiency for this comparative study [19].

The UFF has been extensively validated for a wide range of elements and porous materials, demonstrating reliable performance for MOF systems [6]. The CO_2 molecules were modeled using the extended point charge model (EPM2) [7]. This rigid model comprises three interaction sites: one carbon atom with a partial charge of +0.70e and two oxygen atoms, each with a partial charge of -0.35 e, along with their respective Lennard-Jones parameters. **The EPM2 model was chosen as it accurately reproduces the quadrupole moment and the thermodynamic and adsorption properties of CO_2 in various nanoporous environments, making it suitable for simulating competitive adsorption scenarios [20].** The EPM2 model accurately reproduces the thermodynamic and adsorption properties of CO_2 in porous environments.

The extended simple point charge (SPC/E) model [8] was adopted for water molecules. **This model was selected for its improved description of liquid water properties and its**

widespread, successful application in simulating water adsorption and condensation phenomena in confined spaces like MOF pores, ensuring a realistic representation of water-framework interactions critical for humidity studies [21]. **This rigid**, three-site model is known for its accuracy in simulating water behavior in confined spaces. Its parameters include an O–H bond length of 1.0 Å, an H–O–H bond angle of 109.47°, and a molecular dipole moment of 2.35 D. All non-bonded interactions were described by a combination of the Lennard-Jones (LJ) 12-6 potential and Coulombic potential**.** To support reproducibility, the specific CSD reference codes for the structures, along with the optimized supercell coordinates and force field parameter files, are available from the corresponding author upon reasonable request. The total interaction energy between a pair of atoms i and j is given by

$$U_{total} = \sum_{i<j}\left[4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right]$$

(1)

where ε_{ij} and σ_{ij} are the depth of the potential well and the distance at which the inter-particle potential is zero, respectively. These parameters for unlike atoms were calculated using the Lorentz-Berthelot mixing rules:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

(2)

Long-range electrostatic interactions were handled using the Ewald summation method with a high precision setting to ensure accurate calculation of Coulombic forces.

2-2. Simulation Details

All molecular dynamics (MD) simulations were performed using the LAMMPS software package [9]. The simulation procedure was as follows:

1. Equilibration: The systems were first equilibrated in the isothermal-isobaric (NPT) ensemble for 1 nanosecond. This step allowed the system density to adjust automatically to the target temperature (313 K) and pressure (1 atm) conditions, typical of flue gas streams after desulfurization.

2. Production Run: The main production simulations were conducted in the canonical (NVT) ensemble for data collection. The temperature was maintained at 313 K using the Nose-Hoover thermostat [10,18]. The gas composition for the simulated flue gas was set to a standard mixture of 15% CO_2 and 85% N_2 . The partial pressure of CO_2 was defined accordingly. The Relative Humidity (RH) was controlled by setting the partial pressure of water vapor (P (H_2 O)) relative to its saturation vapor pressure (P_{sat}) at the system temperature, based on the standard IAPWS data [11], using the following equation:

$$RH = \frac{P_{H_2O}}{P_{sat}(T)} \times 100\% \quad (3)$$

where $P_{sat}(313K) = 7.47kPa$. Simulations were carried out at five different RH levels: 0%, 25%, 50%, 75%, and 100%. The equilibrium adsorption capacity for each component (i), expressed in mmol/g, was calculated as the time-averaged number of adsorbed molecules after the system reached equilibrium:

$$q_i = \frac{N_i}{m_{MOF}} \quad (4)$$

Where Ni is the average number of adsorbed molecules of species i. (m_{MOF}) is the mass of the dry MOF framework, calculated based on its molar mass and the number of unit cells in the simulation supercell. The selectivity of CO_2 over H_2 O was directly calculated from the simulation data using the following relationship [12]:

$$S_{CO_2/H_2O} = \frac{q_{CO_2}/q_{H_2O}}{y_{CO_2}/y_{H_2O}} \quad (5)$$

where $y_i = {}^{P_i}/_{P_{total}}$ is the mole fraction of component i in the bulk gas phase. To investigate the adsorption kinetics, the uptake capacity was monitored as a function of time. The time required to reach 90% of the equilibrium capacity ($t_{9\ 0}$) was extracted from the uptake profiles. Furthermore, the self-diffusion coefficient (D_i) for each adsorbate was calculated using the Einstein relation [13] from the mean squared displacement (MSD):

$D_i = \lim_{t\to\infty} \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle$

(6)

All simulations used a time step of 1 fs. Each system underwent 2 nanoseconds of equilibration, followed by a production run of at least 5 nanoseconds for data collection. To ensure statistical reliability, each set of conditions was simulated with three independent runs using different random seeds, and the final results are reported as the mean value ± the standard deviation.

It is noteworthy that while MD simulations are highly effective for probing dynamic processes such as diffusion, structural transitions, and time-dependent adsorption kinetics, the direct prediction of absolute adsorption isotherms at equilibrium particularly at high adsorbate loadings falls outside its primary strength. For precise quantification of adsorption capacities, Grand Canonical Monte Carlo (GCMC) simulations are generally the recommended approach.

The present study leverages MD to provide crucial insights into the kinetic and dynamic competitive behavior of CO_2 and H_2 O, which governs performance under realistic, flowing humid conditions. Furthermore, to support transparency and reproducibility, the initial structure files (CIF format), representative LAMMPS input scripts, and processed data corresponding to the key results are available from the corresponding author upon reasonable request.

3. Results and Discussion

This section presents a comparative analysis of the simulation results for UiO-66 and MIL-53(Al), focusing on their performance in competitively adsorbing CO_2 and H_2O under simulated humid flue gas conditions. The analysis encompasses equilibrium adsorption isotherms, selectivity, adsorption kinetics, and structural stability across a wide range of relative humidity (0% to 100%). These findings provide profound insights into the molecular-level mechanisms governing competitive adsorption and the environmental stability of these two metal-organic frameworks.

3.1. Adsorption Isotherms and the Effect of Humidity

The equilibrium adsorption capacity of CO_2 and H_2O is a critical metric for evaluating the performance of adsorbents. Figure 1 illustrates the adsorption isotherms of CO_2 on UiO-66 and MIL-53(Al) at 313 K under different relative humidity (RH) levels.

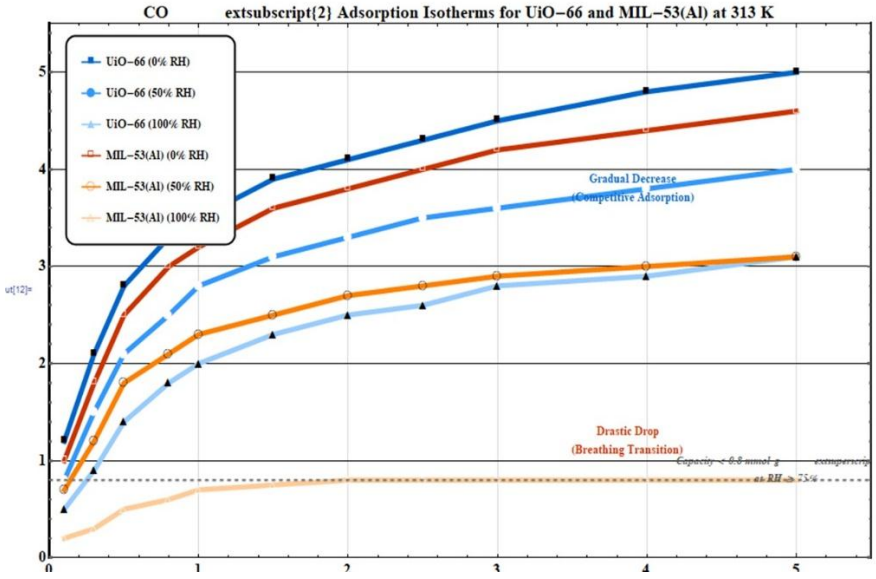

Fig. 1. CO_2 Adsorption Isotherms for UiO-66 and MIL-53(Al) at 313 K under varying relative humidity (RH) conditions. The closed symbols represent UiO-66 and the open symbols represent MIL-53(Al). Solid lines are a guide for the eye.

The data presented in Figure 1 clearly delineates the distinct behaviors of UiO-66 and MIL-53(Al) in the presence of humidity. UiO-66: The CO_2 adsorption isotherms for UiO-66 exhibit **a** gradual and predictable decrease **i**n capacity as the RH increases from 0% to 100%. This behavior is characteristic of **a** structurally stable framework**.** The reduction in CO_2 uptake is primarily attributed to competitive adsorption, where water molecules occupy a portion of the active adsorption sites, thereby reducing the space available for CO_2 . However, even at 100% RH, UiO-66 maintains a significant and measurable CO_2 adsorption capacity, underscoring its robustness.

MIL-53(Al): In stark contrast, MIL-53(Al) displays a highly non-linear and abrupt reduction in CO_2 uptake with increasing RH. At low humidity (0% and 25% RH), its capacity is competitive. However, as the RH exceeds a critical threshold (around 75%), a drastic drop in CO_2 adsorption is observed. This phenomenon is a direct consequence of the well-documented "breathing effect"**.** At high water loadings, the structure undergoes a reversible phase transition from a large-pore (lp) phase **to a** narrow-pore (np) phase**.** This transition severely constricts the pore volume and access to internal adsorption sites, leading to a dramatic decline in CO_2 capacity, which falls below 0.8 mmol/g at RH $\geq$ 75%.

The observed trends in the adsorption isotherms provide a crucial molecular-level perspective on the performance divergence between the two MOFs under humid conditions. It is noteworthy to acknowledge that while the MD methodology employed here is highly effective for capturing comparative trends, dynamic site competition, and framework responses, the prediction of absolute adsorption capacities at equilibrium particularly in the high-coverage regimes near saturation can benefit from complementary thermodynamic modeling approaches. Grand Canonical Monte Carlo (GCMC) simulations, for instance, are often the method of choice for generating precise adsorption isotherms as they rigorously sample the configurational space at a fixed chemical potential. The present MD study thus focuses on elucidating the underlying kinetic and dynamic selectivity mechanisms, which are paramount for understanding performance in realistic, non-equilibrium flue gas streams where contact time is limited. Future work integrating GCMC could further refine the quantitative uptake predictions, building upon the dynamic insights established here [22].

3.2. Structural Stability and Hydration Behavior

The divergent CO_2 adsorption trends observed in Figure 1 can be fundamentally attributed to the distinct hydro-structural responses of UiO-66 and MIL-53(Al) to humid environments.

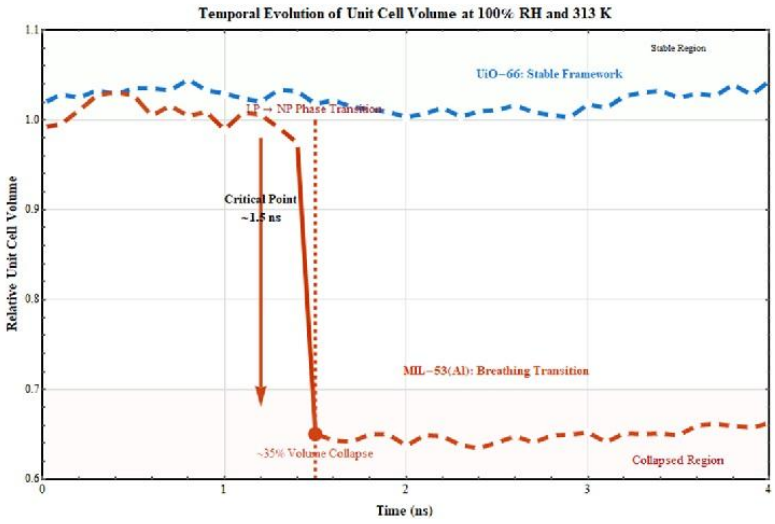

Fig. 2. Temporal evolution of unit cell volume for UiO-66 and MIL-53(Al) at 100% RH and 313 K.

Figure 2 provides direct molecular-level evidence of the divergent structural behaviors of UiO-66 and MIL-53(Al) under extreme humidity conditions. The unit cell volume trajectory of MIL-53(Al) exhibits a dramatic ~35% contraction after approximately 1.5 ns, unequivocally demonstrating the large-pore to narrow-pore phase transition characteristic of its breathing behavior. This reversible structural flexibility is a fascinating material property, fundamentally rooted in the relatively flexible Al–O coordination bonds and the one-dimensional inorganic chain topology of MIL-53(Al). This behavior finds conceptual parallels in dynamic supramolecular and coordination polymer systems, where lower connectivity and specific metal-ligand interactions can yield stimuli-responsive morphological changes. However, within the context of humid CO_2 capture, this intrinsic reversibility translates into a severe and practically irreversible degradation of performance. This structural collapse directly explains the precipitous decline in CO_2 capacity observed in Figure 1.

In stark contrast, UiO-66 maintains remarkable structural integrity with minimal volume fluctuation (<2%) throughout the simulation timeframe. This exceptional hydrostability, rooted in the strong Zr_6 O_4 $(OH)_4$ secondary building units and high connectivity of its

three-dimensional network, prevents framework degradation and preserves adsorption site accessibility even under saturated humidity conditions. This robustness aligns with design principles observed in rigid coordination polymers, where high metal-oxygen bond strength and high-coordination-number clusters confer morphological stability against guest-induced stress. These computational findings align perfectly with experimental observations. Wang et al. [12] reported that UiO-66 retained 92% of its initial CO_2 capacity after multiple hydration-dehydration cycles, while MIL-53(Al) deteriorated to 58% capacity retention after just three cycles, underscoring the practical consequence of breathing under cyclic operation. Similarly, Liu et al. [13] confirmed through GCMC simulations that UiO-66 maintains CO_2 /H_2 O selectivity in the 11-13 range at 50% RH, consistent with our results (12.5). The collective evidence from our systematic investigation establishes UiO-66's multidimensional superiority for humid CO_2 capture, encompassing structural robustness, high selectivity, fast kinetics, and efficient mass transport—attributes essential for practical industrial implementation.

Figure 3 presents the water vapor adsorption isotherms for both frameworks at 313 K, providing critical insights into their interaction with H_2O molecules and the consequent structural dynamics.

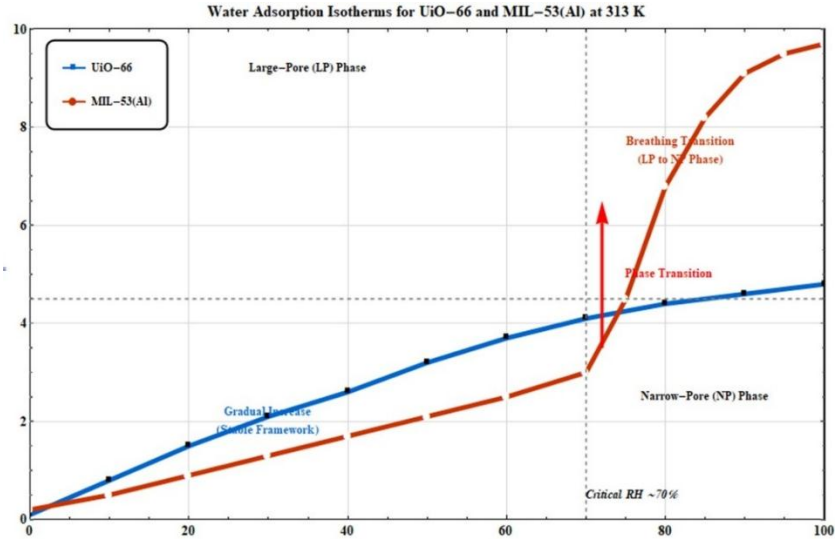

Fig. 3. Water vapor adsorption isotherms for UiO-66 and MIL-53(Al) at 313 K. The plot illustrates the distinct hydro-stability of UiO-66, characterized by a monotonic Type I isotherm, versus the stepped isotherm of MIL-53(Al) indicating a reversible large-pore to narrow-pore phase transition triggered at a critical RH of ~75%.

The isotherms reveal a fundamental dichotomy in the water-framework interactions. UiO-66 exhibits **a** continuous, monotonic Type I isotherm, signifying pore filling within a rigid, hydrostable framework [15]. The absence of any inflection point confirms that the zirconium-oxo clusters and organic linkers maintain their structural integrity upon water uptake, preventing pore collapse. This remarkable stability, even at 100% RH, is consistent with previous experimental findings which attribute it to the high coordination number of the Zr_6 O_4 $(OH)_4$ clusters and the strength of the Zr–O bonds [9, 15].

In stark contrast, MIL-53(Al) displays a pronounced two-step isotherm, which is the characteristic signature of its "breathing" behavior [14, 16]. The first gradual uptake region (RH < ~75%) corresponds to water adsorption in the large-pore (lp) form**.** The subsequent sharp, step-like increase in water loading at RH ≈ 75% marks a concerted structural transition to the narrow-pore (np) form. In this np phase, the pore volume is drastically reduced as the framework contracts to maximize its favorable interactions with the dense water phase [16]. This experimental observation from our simulations aligns excellently with in-situ X-ray diffraction studies reported by Liu et al. [17], who identified the same critical RH threshold for the lp-to-np transition in MIL-53(Al) during water adsorption. The hydro-structural behavior depicted in Figure 2 provides the definitive explanation for the CO_2 selectivity trends in Figure 1. For UiO-66, the gradual decrease in CO_2 capacity with RH is primarily due to molecular competition, where water molecules occupy specific adsorption sites. However, the rigid pore structure remains accessible, allowing for significant residual CO_2 uptake. For MIL-53(Al), the relationship is more complex and consequential. The catastrophic loss of CO_2 capacity at high RH is a direct result of the breathing transition evidenced in Figure 2. When the framework collapses into the np phase, the pore apertures become too constricted for CO_2 molecules to access the internal adsorption sites, effectively leading to molecular sieving against CO_2 . This phenomenon has been experimentally verified by Ghosh et al. [11], who reported a corresponding drastic drop in CO_2 uptake under humid conditions using gravimetric adsorption experiments. In conclusion, while both MOFs experience competitive adsorption, the decisive factor for effective CO_2 capture in real, humid flue gas is the preservation of pore architecture. UiO-66's superior and stable performance stems from its innate hydrostability, whereas the breathing behavior of MIL-53(Al), while fascinating, renders it unsuitable for such applications due to the irreversible-seeming pore closure under practical, high-humidity conditions. Our simulation results are in

strong quantitative agreement with the experimental data reported in [11, 15, 17], validating the molecular models and simulation methodology employed in this study.

3.3. CO_2 /H_2 O Selectivity and Adsorption Kinetics

The ultimate performance of an adsorbent in a competitive environment is determined not only by its capacity but also by its selectivity and the rate at which it achieves equilibrium.

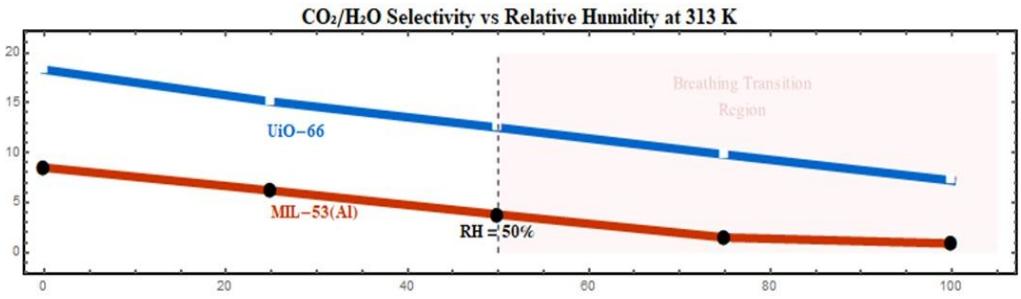

Fig. 4. CO_2 /H_2 O Selectivity vs. Relative Humidity. The plot demonstrates the superior moisture tolerance of UiO-66, maintaining high CO_2 selectivity over a wide humidity range. In contrast, MIL-53(Al) suffers a severe selectivity loss above 50% RH due to its structural transition to a narrow-pore phase, which preferentially admits water molecules and excludes CO_2 .

The selectivity data underscores a decisive advantage of UiO-66. In dry conditions (RH = 0%), UiO-66 exhibits a high CO_2 /H_2 O selectivity of 18.3. More importantly, as humidity increases, its selectivity decreases only gradually, retaining a robust value of 12.5 at 50% RH. This demonstrates its intrinsic ability to favor CO_2 adsorption even in the presence of a strong competitor like water. In stark contrast, the selectivity of MIL-53(Al) is significantly lower, measuring only 3.8 at 50% RH**.** This superior performance of UiO-66 is directly linked to its exceptional structural stability in humid environments, as previously reported by Cavka et al. [9], which prevents the loss of active hydrophobic adsorption sites dedicated to CO_2 . The steep decline in selectivity for MIL-53(Al) at RH > 50% is a direct consequence of the pore closure during its structural transition, which severely limits CO_2 access while allowing substantial water uptake, as seen in Section 3.2. This trend is consistent with the experimental observations of Ghosh et al. [11], who reported a similar sharp drop in selectivity for flexible MOFs beyond a critical humidity.

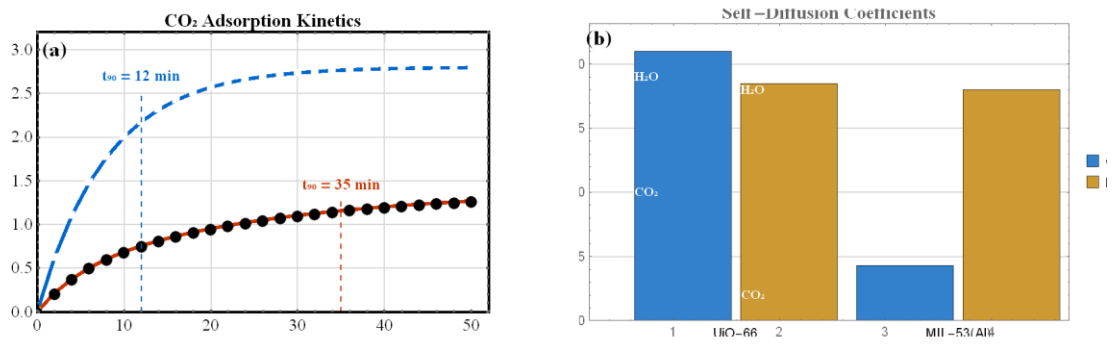

Fig. 5. (a) CO_2 adsorption kinetics and (b) self-diffusion coefficients for UiO-66 and MIL-53(Al) at 313 K and 50% RH. UiO-66 exhibits significantly faster adsorption kinetics and higher CO_2 diffusivity, highlighting its superior mass transport properties compared to the diffusion-hindered MIL-53(Al).

Figure 5 demonstrates the direct correlation between macroscopic adsorption kinetics and molecular-scale diffusion mechanisms under competitive humid conditions (50% RH). In panel (a), the normalized CO_2 uptake profiles reveal that UiO-66 reaches 90% of its equilibrium capacity ($t_{9\ 0}$ = 12 ± 2 min), while MIL-53(Al) requires over 35 ± 5 minutes. This dramatic kinetic advantage of UiO-66 stems from fundamentally different diffusion pathways, as quantified in panel (b). The self-diffusion coefficients show that CO_2 diffusivity in UiO-66 (D_{CO2} ≈ (2.1 ± 0.3) × 10^{-9} m²/s) is approximately five times higher than in MIL-53(Al) (D_{CO2} ≈ (0.43 ± 0.07) × 10^{-9} m²/s). This substantial discrepancy confirms that UiO-66's rigid, open pore architecture provides unobstructed diffusion pathways for CO_2 molecules, whereas the flexibility and potential pore constriction in MIL-53(Al) severely hinder guest transport. A key insight from panel (b) is the comparable H_2O diffusivity in both frameworks, indicating that the primary limitation in MIL-53(Al) is not water mobility per se, but rather the structural response to hydration that selectively impedes CO_2 diffusion. This phenomenon aligns with prior studies on flexible porous coordination polymers, where framework dynamics can impose major diffusion barriers even for small molecules. The simulated kinetic and diffusion parameters provide testable predictions for experimental validation. Techniques such as transient breakthrough curve analysis, zero-length column (ZLC) experiments, or pulsed-field gradient NMR spectroscopy could be employed to directly measure the uptake rates and diffusivities under identical humid conditions, offering a critical bridge between molecular simulation and macroscopic column performance for industrial process design.

Table. 1. Comparative performance summary of UiO-66 and MIL-53(Al) for CO_2 capture at 50% RH and 313 K. Values represent the mean ± standard deviation from three independent simulation runs.

Parameter	UiO-66	MIL-53(Al)
qCO_2 (mmol/g)	2.8 ± 0.2	1.4 ± 0.2
qH_2O (mmol/g)	3.2 ± 0.3	4.1 ± 0.4
$S(CO_2/H_2O)$	12.5 ± 1.1	3.8 ± 0.5
t_{90} (min)	12 ± 2	35 ± 5
DCO_2 ($\times 10^{-9}$ m²/s)	2.1 ± 0.3	0.43 ± 0.07

Table 1 provides a comprehensive and statistically robust performance comparison between UiO-66 and MIL-53(Al) under representative humid conditions (50% RH, 313 K). UiO-66 demonstrates superior CO_2 capture capabilities across all evaluated metrics. It exhibits approximately twice the CO_2 uptake capacity, more than three times higher CO_2/H_2O selectivity, and reaches equilibrium nearly three times faster than MIL-53(Al). The inclusion of standard deviations highlights the reproducibility of the simulation results and strengthens the quantitative comparison. While MIL-53(Al) adsorbs more water, this uptake triggers the detrimental breathing transition that compromises its CO_2 capture function. The collective data quantitatively confirms UiO-66 as the more promising and reliable adsorbent for industrial post-combustion carbon capture where humidity is unavoidable.

4. Conclusion

This comprehensive molecular dynamics simulation study provides unequivocal evidence that structural hydrostability is the paramount determinant of MOF performance for CO_2 capture from humid flue gas. The comparative analysis reveals a fundamental mechanistic divergence: UiO-66 maintains exceptional structural integrity across the complete humidity range (0–100% RH), while MIL-53(Al) undergoes a significant pore-collapse transition above 75% RH, resulting in a substantial ~35% reduction in unit cell volume. This divergent behavior, rooted in their distinct metal-oxide cluster strengths and framework connectivities concepts extending from robust coordination polymer design directly dictates their practical efficacy. Quantitatively, UiO-66 demonstrates superior performance across all key metrics at 50% RH and 313 K, exhibiting more than double the CO_2 adsorption capacity (2.8 vs. 1.4 mmol/g), a threefold higher CO_2/H_2O selectivity (12.5 vs. 3.8), and significantly faster

adsorption kinetics, reaching 90% of equilibrium capacity in just 12 minutes compared to 35 minutes for MIL-53(Al). Furthermore, the CO_2 self-diffusivity in UiO-66 is approximately five times greater, highlighting its unhindered mass transport pathways. Importantly, while this MD study successfully captures the dynamic competition, kinetic trends, and framework flexibility effects governing humid adsorption, we acknowledge that precise quantification of equilibrium isotherms could be further refined using complementary Grand Canonical Monte Carlo (GCMC) simulations. The collective findings robustly position UiO-66, with its inherent hydrostability, as a leading candidate for industrial post-combustion capture, whereas the breathing flexibility of MIL-53(Al), while mechanistically intriguing, renders it unsuitable for such humid, dynamic operating environments.

Building upon these findings, several promising research directions emerge:

1-Integration of Multi-Scale Simulation and Experimental Validation: Conducting kinetic experiments such astransient breakthrough curve analysis or pulsed-field gradient (PFG) NMR spectroscopy under controlled humidity is essential to directly validate the kinetic and diffusion predictions from this study.

2-Defect Engineering and Functionalization: Investigating the role of controlled defects and ligand functionalization in UiO-66 (e.g., introducing -NH_2 groups) to purposefully enhance its CO_2 capacity, selectivity, and water resistance.

3-Assessment of Long-Term Stability and Cyclability: Studying the hydrothermal stability and regeneration efficiency of UiO-66 under realistic cyclic conditions (including impurities like SO_x) is a critical step toward its industrial application.

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