

Abnormal CO₂ and H₂O Diffusion in CALF-20(Zn) Metal–Organic Framework: Fundamental Understanding of CO₂ Capture

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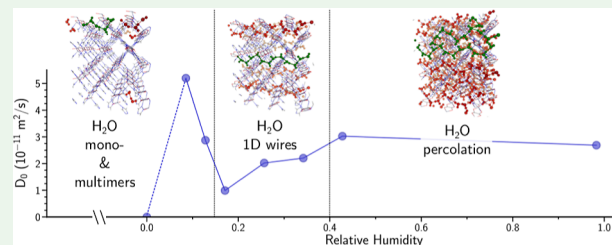
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ABSTRACT: Carbon mitigation is one challenging issue that the world is facing. To tackle the deleterious impacts of CO₂, processes emerged, including chemisorption from amine-based solvents and, more recently, physisorption in nanoporous solids. Physisorption in metal–organic frameworks (MOFs) is currently attracting considerable attention; however, the selection of the optimum sorbent is still challenging. While CO₂ adsorption by MOFs has been widely explored from a thermodynamics standpoint, dynamical aspects remain less explored. CALF-20(Zn) MOF was recently proposed as a promising alternative to the commercially used CO₂ 13X zeolite sorbents; however, an in-depth understanding of the nanoscopic mechanisms originating its good performance still has to be achieved. To do so, we deliver some insights into the adsorption and diffusion of CO₂, H₂O, and mixtures in CALF-20 through atomistic simulations. CALF-20(Zn) was revealed to exhibit unconventional guest–host behaviors that give rise to abnormal guest thermodynamics and dynamics. The hydrophobic nature of the nanoporous solid leads to a low water adsorption enthalpy at low loading, followed by a continuous increase, driven by strong water hydrogen bonds, found to arrange as quasi 1D molecular wires in MOF nanoporosity, recalling water behavior in small-diameter carbon nanotubes. While no superdiffusion was found in the CALF-20(Zn) as compared to carbon nanotubes, this behavior was shown to impact the guest-loading diffusion coefficient profile, with the presence of a minimum that correlates with the inflection point in the adsorption isotherm corresponding to the H₂O wires formation. Interestingly, the diffusion coefficients of CO₂ and H₂O were also found to be of the same order of magnitude, with similar nonlinear profiles as a function of the guest loading. We further demonstrated that the diffusion coefficient for CO₂ in the presence of water decreases with increasing water loading.

KEYWORDS: metal–organic framework, CALF-20(Zn), adsorption, diffusion, carbon dioxide, water, atomistic simulation, carbon capture



INTRODUCTION

Fossil carbon avoidance, greenhouse gas compensation, carbon capture, etc., are important puzzle pieces in the current carbon reduction strategy.¹ However, carbon capture processes² represent an expensive brick in carbon management chains such as CCS (carbon capture and storage) or CCU (carbon capture and utilization), still limiting their massive deployment worldwide. Significant research and development is thus devoted to finding economic alternatives to the canonical amine scrubbing technique, where the thermal regeneration step tends to be highly energy consuming.³ The physisorption technique is currently of interest, although it equally suffers from its own disadvantages, such as insufficient CO₂ product purity. To overcome such a limitation, research relates to intensification by developing rapid capture processes. Indeed, physisorption can be accelerated with minute–long cycles in both rapid-PSA (pressure swing adsorption) and rapid-TSA (temperature swing adsorption) processes.^{4,5} In these techniques, it is key to gain insight into the CO₂ adsorption mechanisms at the atom scale, not only from a thermodynamics point of view but also from a diffusion standpoint,

which is more rarely considered,⁶ although this is an important parameter in CO₂ capture from flue gas and from air. In addition, these carbon capture processes most often operate in the presence of humidity, and there is also a critical need to understand the water adsorption and diffusion in the selected sorbents.^{7–11} More generally, many adsorption processes, especially rapid capture technologies, require efficient molecular transport in order to reach sorbent equilibrium in a limited time.¹² Up to now, diffusion resistances through scales being in nano-, meso-, and macropores^{13,14} (in addition to the role of sorbent surfaces^{12,15,16}) are still elusive, and diffusion phenomena through pore scales (from the nano to the macroscale) in shaped MOF sorbents¹⁷ still need to be more intensively explored.^{18–20} While continuum approaches can be

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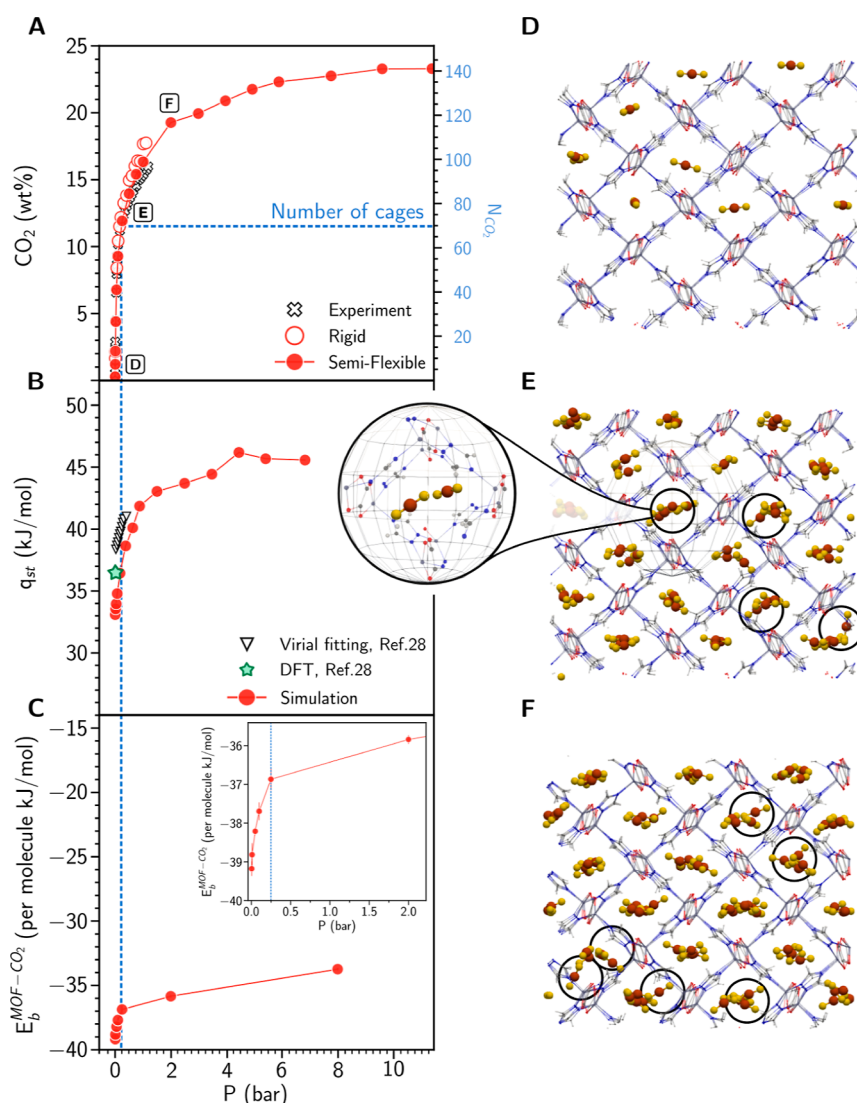


Figure 1. (A) CO_2 adsorption isotherm at $T = 293.15$ K. Red circles correspond to GCMC simulations; open cross symbols correspond to experiments.³⁰ The horizontal dashed blue line corresponds to the total number of cages in the MOF atomistic structure, and the vertical one corresponds to the pressure at which all cages are filled by one CO_2 molecule. (B) CO_2 isosteric enthalpy of adsorption at $T = 293.15$ K. The green star corresponds to density functional theory,³⁰ and the open triangles correspond to the enthalpy of adsorption from the virial fitting method.³⁰ (C) Per molecule, MOF- CO_2 binding energy. The inset corresponds to a zoom of the figure. (D–F) Illustration of the preferential arrangements of CO_2 molecules simulated by GCMC in CALF-20 at different pressures: $P = 3 \times 10^{-3}$ bar (D), 0.5 bar (E), and 2 bar (F). Black circles correspond to cages occupied by more than one CO_2 molecule. The inset shows a zoomed-in view of two CO_2 molecules occupying one cage in the configuration (E).

used for modeling convective fluid flow in macropores,^{21,22} diffusion in angstrompores (*i.e.*, subnanopores with sizes of about a few molecular diameters) is a recent field of research,^{23,24} presenting unexpected and counterintuitive physicochemical behaviors.^{25–29} Herein, we explored in depth the diffusion of CO_2 (in both dry and wet conditions) and H_2O in CALF-20(Zn), a prototypical nanoporous MOF recently reported by Shimizu et al.³⁰ This MOF structure is made of 1,2,4-triazolate-bridged zinc(II) ion layers pillared by oxalate ions to form a three-dimensional lattice encompassing a pore size of 0.6–0.7 nm, Figure S1. Thanks to its stability to humidity, its ability to capture CO_2 from wet flue gases (in the presence of other harsher contaminants, NO_x and SO_x), and its rather simple and cheap synthesis,³⁰ CALF-20 was demonstrated to be a robust alternative sorbent to the currently used zeolite 13X,³¹ even in the presence of relative humidity below 40%.

From a process perspective, this observation paves the way toward the implementation of CALF-20 in a moisture swing or humidity swing technology, as already proposed by the company Svante in their rapid TSA process.^{2,32} However, so far, there is still a lack of understanding of the mechanisms at the origin of this excellent level of performance.³³ Therefore, this calls for an in-depth atomistic exploration of the thermodynamics and kinetics of both CO_2 and H_2O in CALF-20. To address this objective, we deployed a combination of force field-based grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) approaches that revealed rather unusual adsorption and diffusion mechanisms for both guests. Typically, the first CO_2 molecules were found to be adsorbed in the center of the pores rather than at specific sites close to pore walls or metal centers,³⁰ while water was shown to form quasi 1D molecular wires

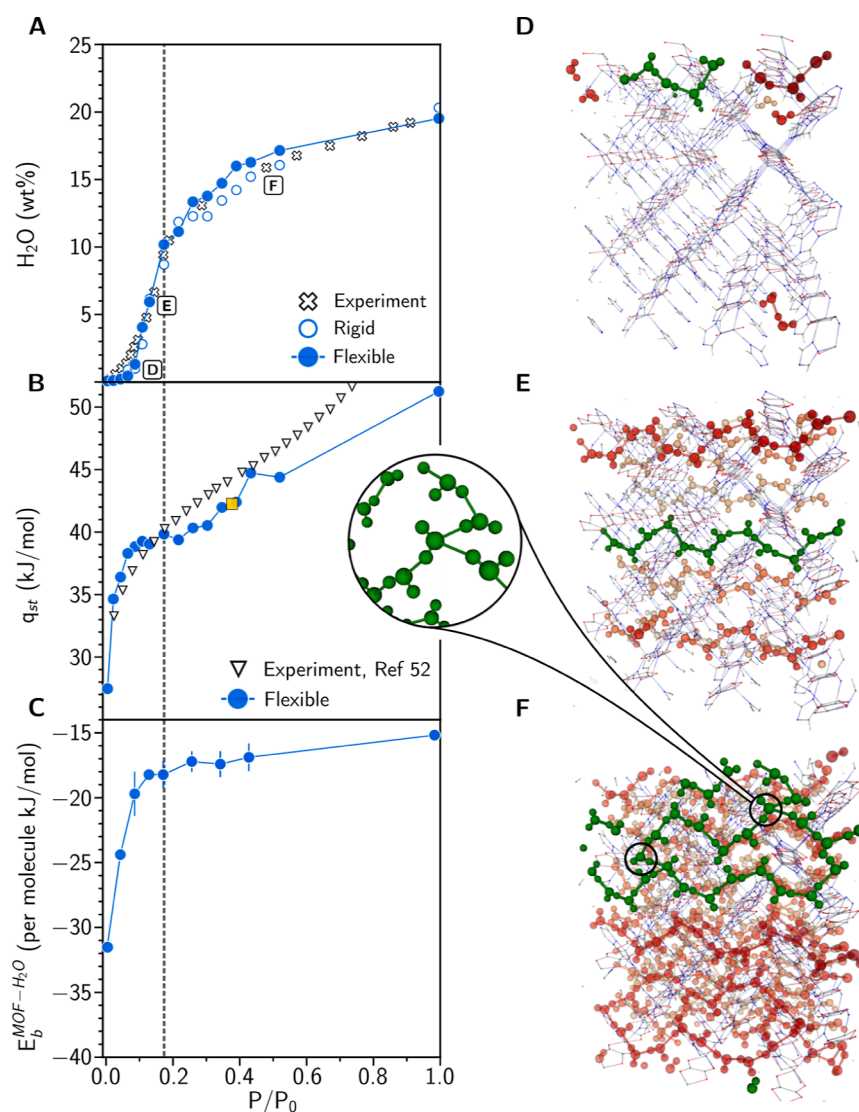


Figure 2. (A) Water adsorption isotherm at $T = 293.15$ K. Blue circles correspond to simulations, and open cross symbols to experiments.³⁰ (B) Water isosteric enthalpy of adsorption at $T = 293.15$ K. The open triangle corresponds to experiments,⁵⁵ and the yellow square corresponds to the experimental enthalpy of adsorption for CO₂ at $P_{\text{CO}_2} = 1$ bar. (C) Per molecule MOF-H₂O binding energy. (D–F) Illustration of the preferential arrangements of water molecules simulated by GCMC calculations in CALF-20 at different P/P_0 (with $P_0 = 0.0234$ bar). (D) $P/P_0 = 0.05$, water molecules are found to be isolated or to form multimers through hydrogen bonds. For visibility, each molecule of multimers was colored depending on their positions on the x axis. (E) $P/P_0 = 0.15$, water molecules start arranging as wires crossing the MOF cages. Each water molecule presents two H bonds, leaving one H-dangling bond. (F) $P/P_0 = 0.5$, wires branching throughout the MOF porosity. The green chain is made of several wires interconnected by water molecules with hydrogen bonds (black circles). The inset presents a zoomed-in view of a water molecule interconnected by different wires.

rather than clusters, recalling the water arrangement in single-wall carbon nanotubes with a diameter below 1 nm.^{34–36} Further, we reveal that both the self- and corrected diffusion coefficients are of the same order of magnitude for the two guest molecules, and interestingly, their concentration dependence follows an unconventional nonlinear trend. A better understanding of such unusual properties may allow one to improve process modeling and help in formulating next-generation polymorphic structures that may improve CO₂ uptake and reducing carbon capture cost.

METHODS

A supercell model of CALF-20 made of $4 \times 3 \times 3$ unit cells Figure S1 was considered for all GCMC and MD simulations. The MOF framework was treated as flexible (*i.e.*, each atom of the MOF is free

to move under thermal excitations, while the MOF volume is kept constant) for both thermodynamics and kinetics studies, using the universal force field UFF³⁷ for the intramolecular bonding, bending, and dihedral terms to describe the MOF framework. In this later case, this is even more important since it is well documented that the consideration of the flexibility of the porous solid structure can be of utmost importance to describe guest diffusion.^{38–41} It is worth noting that prior to selecting UFF, we compared adsorption isotherms with Dreiding⁴² and UFF4MOF.⁴³ While small differences were obtained on the CO₂ adsorption isotherms using the 3 force fields, UFF was found to enable a better reproduction of the water adsorption isotherm, Figure S2. To gain insight into flexibility effects, adsorption isotherms and diffusion coefficients were also calculated with a rigid framework, considering the pristine structure previously reported by Shimizu et al.³⁰ The CO₂ and H₂O adsorption isotherms and enthalpies of adsorption were determined by GCMC with the LAMMPS code.⁴⁴ For each calculation, deviation from the ideal gas

was corrected from the Soave–Redlich–Kwong model.⁴⁵ Diffusion properties were assessed by MD simulations in the canonical ensemble. The consistency of the diffusion coefficients obtained was verified by calculations performed in both equilibrium and out-of-equilibrium conditions (more detail in [Supporting Information](#)).⁴⁶ All atoms of the MOF framework were treated as charged Lennard-Jones (LJ) interacting sites with LJ parameters taken from UFF.³⁷ The REPEAT model⁴⁷ was used to assign point charges to each MOF atom as it was demonstrated to be well suited to reproduce both CO₂ and H₂O isotherms.³⁰ CO₂ molecules were modeled by the long-range pair potential proposed in,⁴⁸ shown to well reproduce the experimental isotherms at ambient conditions using the CALF-20 structure,³⁰ while water was modeled from the four sites TIP4P-Ew⁴⁹ potential. A 1 nm cutoff was applied for all LJ interactions; in addition, a long-range Coulombic solver (Ewald summation) was considered. Each interatomic LJ parameter (being for MOF/MOF, MOF/guests, and guests/guests) was determined from the Lorentz–Berthelot mixing rule. Simulation details are provided in the [Supporting Information](#).

RESULTS AND DISCUSSION

Single CO₂ Component. The GCMC CO₂ adsorption isotherms, calculated using both rigid (orange open circles) and flexible (orange circles) CALF-20 frameworks at $T = 293.15$ K, were compared to the corresponding experimental data reported elsewhere³⁰ (open cross symbols) in [Figure 1A](#). The simulated isotherms are of the Langmuir type, characteristic of nanoporous adsorbents, with no effect on MOF being considered a rigid or flexible framework. In [Figure 1B](#), we show the isosteric enthalpy of adsorption, which was found to increase as a function of the partial pressure P . This energetic parameter was determined by the fluctuation method

$$q_{\text{st}} = k_{\text{B}}T - \frac{\partial \langle U \rangle}{\partial \langle N \rangle} = k_{\text{B}}T - \frac{\langle UN \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (1)$$

where q_{st} is the isosteric enthalpy of adsorption, k_{B} is the Boltzmann constant, and N and U are the guest number and potential energy, respectively. At highly dilute conditions, the simulated $q_{\text{st}} \sim 35$ kJ/mol, in agreement with the literature (green stars as well as open triangles),³⁰ further increases with the loading at ~ 45 kJ/mol at large P . We have also determined the guest–host binding energy after annealing the system. It is defined as $E_{\text{b}}^{\text{G-H}} = E^{\text{G+H}} - E^{\text{H}} - E^{\text{G}}$, where $E^{\text{G+H}}$ corresponds to the potential energy of the host (H) filled by guest adsorbates (G), E^{H} is the host energy after removing guest molecules, and E^{G} is the energy of guest molecules after removing the host. $E_{\text{b}}^{\text{G-H}}$ thus corresponds to the binding energy of the fluid medium interacting with the pore walls. Below $P \sim 0.25$ bar (dashed blue line in [Figure 1](#)), $E_{\text{b}}^{\text{G-H}}$ is shown to strongly increase (less attractive MOF surfaces), [Figure 1C](#), while q_{st} continuously increases. This behavior is attributed to G–G interactions driving the increase in the overall enthalpy of adsorption. In CALF-20, CO₂ molecules are found to be arranged in the near center of MOF cages,³⁰ [Figure 1D](#). When $P \sim 0.25$ bar, all MOF cages are statistically occupied by one CO₂ molecule, [Figure 1E](#). This is further confirmed by the number of adsorbates found to match the total number of cages (dashed blue line in [Figure 1](#)). At larger pressure, the overall $E_{\text{b}}^{\text{G-H}}$ decreases (less negative energy), corresponding to configurations with additional guest molecules in some cages, [Figure 1F](#). The latter arrangement will be more discussed below in light of the radial distribution function (RDF).

Single H₂O Component. The same GCMC simulations were performed at $T = 293.15$ K for water adsorption. The

H₂O isotherm presents an S-shape, [Figure 2A](#). As for CO₂, the consideration of a rigid (open blue circles) and flexible (blue circles) MOF framework does not lead to differences in the calculated isotherms. At low loading, $q_{\text{st}} \sim 40$ kJ/mol, a value below the water vaporization enthalpy, denoting an hydrophobic nature of the structure, [Figure 2B](#) (further confirmed by the S-shape isotherm). The following increase is thus attributed to G–G interactions, confirmed by the G–H binding energy presenting a smooth increase (less attractive pore surfaces), [Figure 2C](#). At highly dilute conditions, water is shown to adsorb as isolated molecules or small multimers, [Figure 2D](#). When the loading increases, the formation of hydrogen bonds drives the increase in q_{st} ([Figure 2B](#)). However, surprisingly, water molecules are not found to form clusters (as usually reported for many MOF structures,^{10,50–53}) but are arranged as quasi 1D molecular wires propagating through MOF cages, [Figure 2E](#). This molecular arrangement recalls the behavior of water in small-diameter single-wall carbon nanotubes (SWCNT), where 1D water wires were shown to result from strong confinement in highly hydrophobic solid pores, where water/water interactions dominate.⁵⁴ As for water adsorbing in CALF-20 angstrompores, H₂O adsorption in SWCNT shows an increasing q_{st} along with P/P_0 (with $P_0 = 0.0234$ bar), attributed to the formation of a strong water H-bond network.^{34–36} Such a behavior, as shown in the 3D pores of CALF-20, may arise (as for 1D SWCNT) from the relative hydrophobic nature of the MOF, in addition to the high confinement of the MOF cages. Note that the increase of wire number as well as their lengths, along with P/P_0 , may contribute to a smooth decrease in $E_{\text{b}}^{\text{G-H}}$ (less negative) due to the possible uncommensurability of water H-bonds in wires with the pore surface of the MOF. At large P/P_0 , percolation occurs, with neighbor wires found to interconnect, [Figure 2F](#). This behavior is more detailed by the cluster analysis discussed below from MD calculations. It is worth noting that q_{st} for the two guest species (CO₂ and H₂O) present similar values ([Figures 1B](#) and [2B](#)) despite the notable difference in their respective G–H binding energies ([Figures 1C](#) and [2C](#)) attributed to G–G interactions. We can also notice that $q_{\text{st}}^{\text{CO}_2} \sim q_{\text{st}}^{\text{H}_2\text{O}}$ at $P_{\text{CO}_2} \sim 1$ bar and a relative humidity of about 42% (yellow square in [Figure 1B](#)), in agreement with the results already reported³⁰ at 40%.

Single Component Diffusion. MD simulations were further performed to determine the self- and corrected diffusion coefficients, labeled as D_{s} and D_0 , respectively. To do so, we used the mean square displacement, the Green–Kubo relation, and a nonequilibrium molecular dynamics method (NEMD), based on transport theory.²⁵ The different methodologies used and computational details are described in [Figures S3A,B](#) and [S4](#). A comparison of the application of the different approaches is presented in [Figure S5](#), showing the consistency in diffusion coefficients calculated from the different methods. In addition, we also show the minor effect of the CALF-20 force field (UFF and Dreiding) on the diffusion coefficient values in [Figure S6A](#). Note that while MSD and NEMD methods show a reasonable agreement for D_0 , we observed a larger difference from both techniques with the Green–Kubo approach related to the inherent complexity of this latter method.

In order to check the impact of the MOF flexibility on CO₂ diffusion, we then performed calculations in both rigid and flexible frameworks based on the UFF force field, [Figure 3A](#).

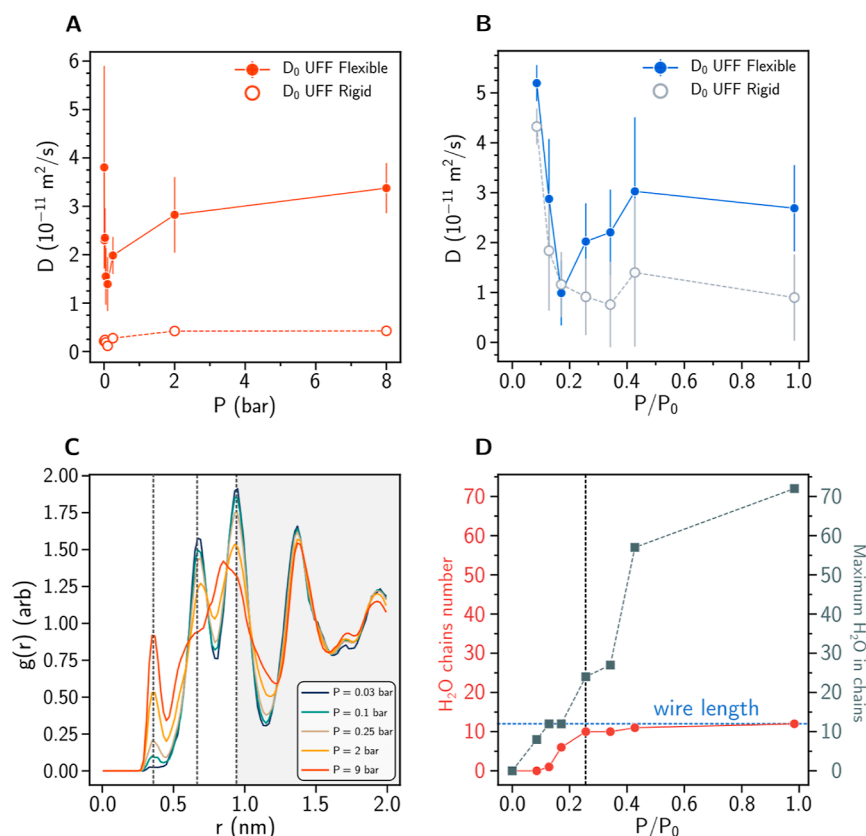


Figure 3. (A) Simulated corrected diffusion coefficient for CO_2 as a function of P . (B) Simulated corrected diffusion coefficient for H_2O as a function of P/P_0 . (C) RDF of the CO_2 center of mass for different partial pressures. The gray background corresponds to the second neighboring area. (D) Water wire analysis, with orange circles corresponding to the number of wires in the structure. The gray squares correspond to the mean number of water molecules per wire, surrounded by the maximum (upper dashed line) and minimum (lower dashed line) numbers of water molecules spanning all wires in the structure. The gray area denotes the gap between the smaller and larger wires in structures.

We thus showed that accounting for thermal effects in the solid tends to boost the CO_2 diffusion (orange circles) by an order of magnitude compared to the rigid approximation (open orange circles). Note that such a behavior has already been reported for several other porous solids.^{38,56} Self- and corrected diffusion coefficients were then compared along with the pressure for the two guest species from MSD and NEMD techniques (more details in Supporting Information). The two diffusion coefficients were found to have the same order of magnitude. Based on the Green Kubo relation, we can express the corrected diffusion coefficient given by

$$D_0 = \frac{1}{dN} \left\{ \sum_{i=1}^N \int_0^\infty \left\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle dt + \sum_{i \neq j}^N \int_0^\infty \left\langle \mathbf{v}_j(t) \cdot \mathbf{v}_i(0) \right\rangle dt \right\} \quad (2)$$

where d is the dimension of the system, N is the number of guests, $\mathbf{v}$ are the velocities of molecules i and j , and angular brackets denote the ensemble average of the velocity correlation. The first summation in (eq 2) corresponds to D_0 , and the second corresponds to the cross correlations. For CO_2 diffusion, the cross term is found to be negligible and $D_s^{\text{CO}_2} \sim D_0^{\text{CO}_2}$, Figure S6A. This behavior originates from the strong guest confinement in CALF-20 angstrom pores, where the G-H interactions dominate as compared to the G-G

interactions. Regarding water molecules, $D_s^{\text{H}_2\text{O}} \sim D_0^{\text{H}_2\text{O}}$ up to $P/P_0 \sim 0.2$ (inflection point in the isotherm), Figure S6B. While water behaves as independent molecules, G-H represent the main interactions (despite a relatively low binding energy), and the limited number of G neighbors does not induce a large cross-correlation effect in eq 2. However, once water wires form ($P/P_0 \sim 0.2$), collective interactions can no longer be neglected, and a moderate deviation can be observed, Figure S6B. The comparison between flexible MOF and rigid MOF frameworks was also considered for the diffusion of water, showing a less pronounced effect compared to CO_2 . A deviation is, however, observed at $P/P_0 \sim 0.2$, suggesting that solid vibrations promote water diffusion when wires are formed, Figure 3B.

$D_0^{\text{CO}_2}$ from NEMD (in flexible MOF) shows a non-monotonic behavior, with a minimum at $P \sim 0.1$ bar. For a $P < 0.1$ bar, a few isolated molecules are shown to interact with low-energy sites of the MOF. Thanks to the large available free pore volume, molecules have a probability to diffusing, hopping from one cage to another. At around 0.1 bar, molecules interact strongly with the MOF pore wall; in addition, the increase of the CO_2/CO_2 interactions leads to a decrease of their diffusion. When $P \sim 0.25$ bar, almost all cages are occupied by one guest molecule (dashed blue line in Figure 1A). In such a configuration, CO_2 molecules are constrained to share a cage with neighboring CO_2 . This situation is thermodynamically not favorable and originates from a decrease of guest mobility, reflected by the minimum in

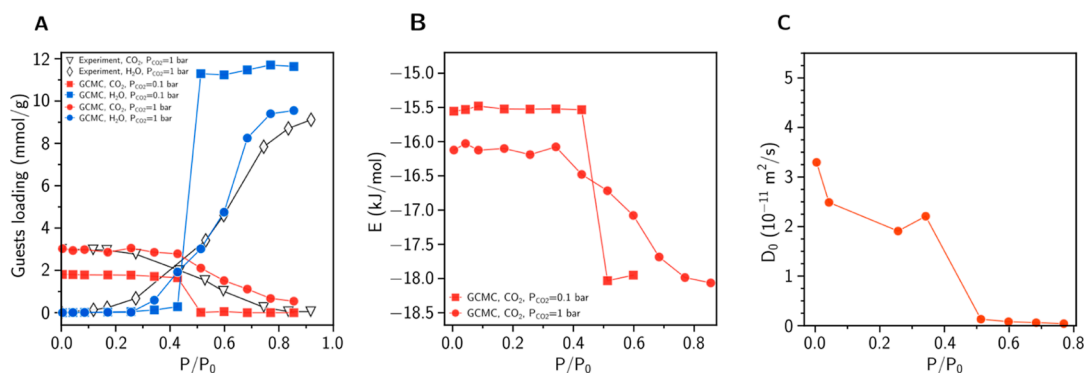


Figure 4. (A) Coadsorption isotherms of CO_2 and H_2O plotted as a function of the relative humidity P/P_0 . The orange and blue circle symbols plots correspond, respectively, to the GCMC CO_2 and H_2O loadings at $T = 293.15$ K and a CO_2 pressure of 1 bar. The open symbols correspond to experiments under the same conditions. The orange and blue square symbols plots correspond, respectively, to the CO_2 and H_2O loadings at $T = 293.15$ K and a CO_2 pressure of 0.1 bar. (B) Per CO_2 molecule, energy is adsorbed in CALF-20 as a function of the relative humidity. The A circle symbols plot corresponds to CO_2 at 1 bar, and squares correspond to CO_2 at 0.1 bar. (C) Corrected CO_2 diffusion coefficients plotted as a function of the relative humidity.

$D_0^{\text{CO}_2}$, Figure 3A. This is confirmed by the slope change shown in $E^{\text{G-H}}$ (vertical dashed blue line in Figure 1C) and by the CO_2 center of mass RDF, Figure 3C. In the RDF, the second and third peaks correspond to CO_2 molecules in first neighbor cages on z and (x, y) directions, respectively, and the gray area corresponds to second neighbor cages. However, the first peak below 0.5 nm corresponds to additional guest molecules in some cages, already hosting one CO_2 molecule, which is further reflected by the increase of the first peak in the RDF along with the partial pressure increase. Hence, above $P \sim 0.1$ – 0.2 bar, some cages are occupied by more than one CO_2 molecule, sharing weaker interactions with solid surfaces and increasing the CO_2 diffusion coefficient. At larger P/P_0 , the corrected diffusivity reaches a constant value, typical of large pore volume occupation, where diffusion is limited by guest collisions.

While water diffusion also presents a minimum at $P/P_0 \sim 0.2$, the mechanisms behind diffusion behaviors are different from those depicted for CO_2 . In Figure 3D, we can observe the evolution of the water wires number (orange circles), as well as their constitutive maximum number of molecules (gray squares). In the atomistic MOF structure used for simulations, a water wire crossing the structure throughout a channel (made of connected MOF cages along one direction) counts 12 water molecules. Thus, water does not present wires below $P/P_0 \sim 0.2$. In this situation, the growth of multimers (<12 water molecules, horizontal dashed line) is accompanied by a decrease in water mobility, with a minimum in diffusion at around $P/P_0 \sim 0.2$ (Figure 3B). At such a pressure, 10 wires are found to occupy the 12 MOF cages, with the wire number reaching a maximum in Figure 3D. At slightly higher pressure (vertical dashed line), additional water molecules are found with extra-hydrogen bonds bridging some molecular wires together (Figure 2E), corresponding to the early stage of the water percolation. These bridging molecules are less stable than ones within a wire, increasing $D_0^{\text{H}_2\text{O}}$. At $P/P_0 \sim 0.4$, wires are largely interconnected through cages (Figure 2F), and water medium is clearly percolated, driving an almost constant diffusion coefficient along with the relative humidity.

Multi Component Mixtures. GCMC simulations were performed to determine the CO_2 – H_2O coadsorption isotherms for CO_2 partial pressures ranging from 0.1 to 1 bar, with relative humidity ranging from 0 to 0.82, Figure 4A. As

already reported in experiments (open triangles and diamonds),³⁰ at $P_{\text{CO}_2} = 1$ bar, simulations show that CO_2 molecules (red circles) favorably adsorbed over H_2O (blue circles) up to $P/P_0 \sim 0.4$, in good agreement with previous experimental data. The transition toward a more favorable H_2O adsorption above 0.4 occurs progressively with a smooth change in the mixture stoichiometry along with $P_{\text{H}_2\text{O}}/P_0$ from ~ 0.25 to 0.7. Following the per atom energy, plotted as a function of $P_{\text{H}_2\text{O}}/P_0$, we show that a few adsorbed molecules have a weak impact on the CO_2 interaction energy below 0.4, while a pronounced decrease is seen above, Figure 4B. Adsorbed water is thus found to act as an additional adsorbing medium (in addition to the CALF-20 framework), increasing the CO_2 stability in the system thanks to the CO_2 – H_2O interactions. However, in CALF-20, such an effect does not promote an increase of CO_2 adsorption, as already noticed in other MOFs.¹⁰ For multicomponent adsorption, although water molecules show wire formation, the percolation threshold found at around $P_{\text{H}_2\text{O}}/P_0 > 0.25$ in a single water component is found to be shifted above 0.4 in the presence of CO_2 . When such a relative humidity condition is reached, the water network made of strong hydrogen bonds is found to occupy a large fraction of the CALF-20 pore volume, allowing the adsorption of only a few CO_2 molecules in the system. For $P_{\text{CO}_2} = 0.1$ bar, the CO_2 is found to compete with water at a slightly smaller relative humidity ~ 0.42 , followed by a sharp drop of the adsorbed CO_2 molecules. This abrupt shift suggests that, compared to $P_{\text{CO}_2} = 1$ bar, where all MOF cages were shown to host at least one CO_2 molecule in the single component case, the collective CO_2 interactions allow to smooth the transition from CO_2 to H_2O adsorption compared to 0.1 bar, Figure 4A, as further confirmed by the per-molecule energy difference at moderate relative humidity shown in Figure 4B. In this latter case, CO_2 molecules share weaker collective interactions, and so the water driving force required to remove CO_2 is smaller and occurs suddenly. In light of such behaviors, we then explored the CO_2 diffusion at $P_{\text{CO}_2} = 0.1$ bar along with the relative humidity, Figure 4C. We found that the diffusion coefficient of CO_2 decreases monotonically when the relative humidity increases. This expected behavior is in fact

driven by the continuous decrease of overall framework porosity along with increasing water density.

CONCLUSIONS

Comparing the two guests, we noticed that $D_0^{\text{CO}_2}$ and $D_0^{\text{H}_2\text{O}}$ present the same order of magnitude, differing from the number of other MOFs, where water usually shows slower mobility compared to CO_2 . This behavior relates to specific properties of CALF-20, where both CO_2 and H_2O show similar enthalpies of adsorption, presenting an increasing trend with gas pressure related to G–G interactions. Besides showing similar isosteric adsorption enthalpy, we revealed that CO_2 adsorption is favored over H_2O below $P/P_0 \sim 0.4$ – 0.5 (in agreement with already reported results.³⁰) At low humidity, water was found as isolated molecules and/or small multimers ($P/P_0 < 0.2$), and unconnected wires ($P/P_0 \sim 0.4$) were found to weakly interact with MOF pore surfaces. In such conditions, CO_2 presenting a smaller enthalpy of adsorption may displace water from CALF-20 angstrom pores. However, when the relative humidity become larger than ~ 0.4 , the water medium was found to form a percolated network. In such an arrangement, water may be blocked through MOF cages, and CO_2 at 1 bar is not able to break water H bonds to diffuse through the water medium adsorbed in the framework porosity. At 0.1 bar, we note that the shift from one guest to another occurs abruptly, while the competing humidity threshold is found to be just slightly lowered compared to that with a CO_2 pressure of 1 bar. This is an interesting result that may suggest that adsorption in CALF-20 at moderate CO_2 partial pressure may allow more efficient desorption in processes where the regeneration step is ensured by water intrusion. Beyond such a mechanistic analysis, CALF-20(Zn) is currently receiving particular attention due to its unconventional physicochemical properties in addition to its simple synthesis. Although this work focuses on the thermodynamics and kinetics of two guest molecules in CALF-20 intrapores, we believe that such atomistic bricks could help in taking advantage of such unconventional behaviors for future applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.3c03752>.

Additional methodological and technical details, including supplementary figures, theoretical details concerning the different diffusion approaches followed in this study, and extended methodological details in numerical simulations as well as a LAMMPS atomistic configurations of the CALF-20(Zn) with a $\text{CO}_2/\text{H}_2\text{O}$ mixture (PDF) (XYZ)

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Notes

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