

Unlocking the Effect of H₂O on CO₂ Separation Performance of Promising MOFs Using Atomically Detailed Simulations

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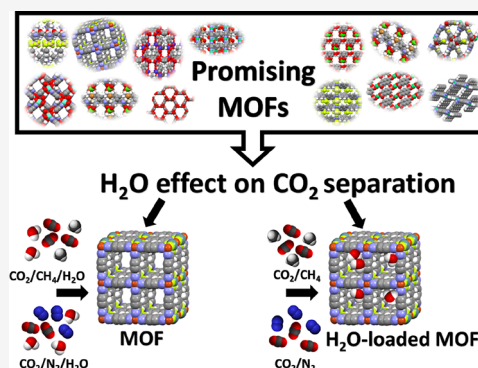
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ABSTRACT: Metal organic frameworks (MOFs) have been considered as potential adsorbents for adsorption-based CO₂/CH₄ and CO₂/N₂ separations because of their high CO₂ selectivities and high working capacities. H₂O in flue gas and natural gas streams affects the gas uptake capacities of MOFs. However, the presence of H₂O is commonly neglected in high-throughput computational screening studies while assessing the CO₂ separation performances of MOFs. In this study, the impact of the presence of H₂O on the CO₂ separation performances of 13 MOFs that were previously identified as the best adsorbent candidates among several thousands of MOFs was examined. Molecular simulations were used to compute selectivity, working capacity, regenerability, and adsorbent performance score (APS) of MOFs considering separation of binary CO₂/CH₄, CO₂/N₂, and ternary CO₂/CH₄/H₂O and CO₂/N₂/H₂O mixtures. The results showed that introduction of H₂O as the third component into binary CO₂/CH₄ and CO₂/N₂ mixtures significantly affected the adsorbent evaluation metrics of MOFs that have strong affinity toward H₂O because of the presence of specific functional groups and/or extra framework anions in the framework. Remarkable increases in CO₂/N₂ selectivities of MOFs were observed in the presence of H₂O. On the other hand, simulations performed using MOFs that are preloaded with H₂O to mimic the exposure of MOFs to humidity prior to gas adsorption revealed drastic decreases in CO₂ working capacities and APSs of MOFs both for CO₂/CH₄ and CO₂/N₂ separations. These results will be useful for the design and development of efficient MOF adsorbents for CO₂ capture under humid conditions.



1. INTRODUCTION

Burning of fossil fuels including coal and natural gas produces most of the carbon dioxide (CO₂) emissions.¹ To reduce CO₂ emissions from coal-fired plants, separation of CO₂ from other gases present in the flue gas, mainly nitrogen (N₂), is significant. Similarly, for natural gas sweetening, removal of CO₂ from methane (CH₄), which is the main component of natural gas, is required to improve the energy content of the natural gas and to prevent corrosion of pipelines. Adsorption-based CO₂ separation techniques have become alternative to traditional methods such as amine scrubbing because of their less complex infrastructures and low energy requirements.² Working capacity, the difference of gas uptakes obtained at adsorption and desorption pressures, and selectivity are the two critical parameters for an adsorption-based gas separation method. Both high working capacity and high selectivity are desired in addition to high regenerability for an efficient and economic gas separation.³

Metal organic frameworks (MOFs) have been widely used as adsorbents for adsorption-based gas separations because of their permanent porosities, large surface areas (SAs), and chemical functionalities.⁴ There are excellent reviews on CO₂ separation performances of MOFs.^{4–8} Several MOFs including Mg-MOF-74, a series of SiF₆²⁻ pillared MOF materials (SIFSIX), and UTSA-48 with amine functionalities were identified as

promising adsorbents because of their high isosteric heats of adsorption for CO₂, leading to high CO₂ selectivities.⁹ Considering the enormous number of experimentally synthesized MOFs in the literature (99075 MOFs according to the November 2019 version of the Cambridge Structural Database, CSD¹⁰), many promising MOF adsorbents for CO₂ capture exist. Herein, molecular simulations play a key role in identifying the best MOFs for CO₂ separations. Grand canonical Monte Carlo (GCMC) simulations which provide the description of the equilibrium of gas mixtures within a solid adsorbent are commonly used to compute CO₂ adsorption in MOFs. High-throughput computational screening methods in which several thousands of MOFs are studied for adsorption of a gas mixture at predetermined conditions have been used to identify the top-performing MOFs. For example, Watanabe and Sholl¹¹ investigated the potential of 1163 MOFs for CO₂/N₂ separation and they found that MOFs with large SAs exhibit high CO₂ uptakes. Wilmer et al.¹² computationally screened >130,000 hypothetical MOFs for CO₂/CH₄ and CO₂/N₂ separations

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under different adsorption and desorption conditions and suggested quantitative structure–property relationships (QSPR) between pore size, SA, pore volume (PV), chemical functionality, and several adsorbent evaluation criteria such as CO₂ working capacity and selectivity. Aghaji et al.¹³ examined >320,000 hypothetical MOFs for CO₂/CH₄ separation using the machine learning techniques and showed that a significant computation time can be saved by using QSPR models and atomically detailed simulations can be then performed for a small fraction of the MOFs. Lin et al.¹⁴ screened thousands of zeolites and zeolitic imidazolate frameworks (ZIFs), a class of MOFs which has the same topology with zeolites, for CO₂ capture. They introduced a new metric, parasitic energy to rank materials for CO₂/N₂ separation based on the energy to heat the material, to supply the heat of desorption, and to pressurize CO₂ to adsorption pressure. Their results showed that materials with high Henry's coefficients of CO₂ exhibit high CO₂ working capacities and low parasitic energies. Qiao et al.¹⁵ screened 4764 computation-ready experimental (CoRE) MOFs¹⁶ for CO₂/CH₄ and CO₂/N₂ separations and found that lanthanide-based MOFs with open metal sites possess the highest separation performance. Our group¹⁷ screened the most recent MOF database integrated within the CSD¹⁰ and identified the best adsorbents for CO₂/CH₄ and CO₂/N₂ separations using molecular simulations. MOFs having isosteric heat of adsorption difference > 30 kJ/mol, 3.8 Å < pore limiting diameter (PLD) < 5 Å, 5 Å < the largest cavity diameter (LCD) < 7.5 Å, 0.5 < porosity < 0.75, SA < 1000 m²/g were found to be the best performing adsorbents for CO₂ separation.

These high-throughput computational screening studies predicted CO₂/CH₄ and CO₂/N₂ adsorption and/or separation performances of large numbers of MOFs in a time-efficient manner. However, the presence of H₂O in the gas mixtures, which may affect the CO₂ adsorption properties of MOFs was not considered because computational modeling of H₂O adsorption using GCMC simulations is costly. Henry's coefficients of H₂O were generally computed to quantify MOF–H₂O interactions and to estimate CO₂/H₂O selectivities at infinite dilution. For example, Li et al.¹⁸ initially computed the Henry's law constants of H₂O and CO₂ to screen the CoRE MOFs for CO₂/H₂O and CO₂/H₂O/N₂ separations where H₂O was treated as the third component of the gas mixture and its partial pressure was fixed during the simulation. They identified the best 15 MOFs which offered the highest CO₂/H₂O selectivity. Li et al.¹⁹ also studied the effect of charge assignment methods on the predicted CO₂/H₂O separation performances of MOFs. Henry's law constants of CO₂ and N₂ were found to be similar but different values were computed for H₂O based on the charge assignment method used in molecular simulations. Coelho et al.²⁰ recently showed that H₂O molecules can be preloaded into MOFs and then the number of adsorbed gas molecules in the framework can be computed. They discussed that this approach has similarities with the experimental procedure in which water was first injected into the material and after equilibration, gas molecules were injected with increasing pressure. CO₂ separation performance of an MOF that is preloaded with H₂O before the adsorption of a gas mixture has not been compared with that of an MOF that is used to separate a gas mixture having H₂O as the third component. This type of comparison is important to assess how the predicted CO₂ separation performances of highly promising MOF adsorbents would change in the presence of H₂O.

In this study, we specifically aimed to understand the impact of H₂O, either in the gas mixture or preloaded into the framework, on the CO₂ separation performances of MOF adsorbents. Performing atomically detailed simulations of H₂O adsorption for several thousands of MOFs is computationally very costly because of the very low acceptance ratios for insertions and deletions of H₂O molecules during the GCMC simulations. Therefore, we focused on the best MOF adsorbents which we previously identified by screening 54808 MOFs for CO₂/CH₄ and CO₂/N₂ separations¹⁷ and examined the effect of the presence of H₂O on the natural gas and flue gas separation performances of the highly promising MOFs. We first studied coadsorption of H₂O with binary CO₂/CH₄ and CO₂/N₂ mixtures. Several adsorbent evaluation metrics such as adsorption selectivity (S_{ads}), working capacity (ΔN), adsorbent performance score (APS), and percent regenerability (R %) were calculated for separation of ternary CO₂/CH₄/H₂O and CO₂/N₂/H₂O mixtures. Coefficient of determination (R^2) was calculated for the adsorbent performance metrics that we separately computed for binary mixture (CO₂/CH₄ and CO₂/N₂) and ternary mixture (CO₂/CH₄/H₂O and CO₂/N₂/H₂O) separations to uncover the impact of H₂O on the CO₂ separation performances of MOF adsorbents. We then studied binary CO₂/CH₄ and CO₂/N₂ mixture adsorption in the promising MOFs that we first loaded with H₂O considering 80% relative humidity. Adsorbent performance evaluation metrics of H₂O-loaded and pristine MOFs were compared to discuss how the CO₂ separation performances of the highly promising MOF adsorbents change when they are exposed to H₂O before the adsorption-based gas separation processes.

2. COMPUTATIONAL METHODS

We first compared our simulations with the available experimental results for single-component H₂O uptake in various MOFs including Cu-BTC,²¹ MOF-5,²² MIL-53(Cr),²³ Mg-MOF-74,²⁴ Ni-CPO-27,²⁵ UiO-66,²⁶ and ZIF-8²⁶ at 298 K, and multicomponent H₂O uptake in a CO₂/N₂/H₂O mixture in Cu-BTC²⁷ and MOF-5²⁷ at 313 K to validate the accuracy of our molecular simulation approach. Crystal structures of these MOFs were taken from the CSD¹⁰ and the solvents in the frameworks were removed using the Python script of the CSD MOF subset.²⁸ After showing the good agreement between our simulation results and experimentally reported H₂O uptakes, we applied the same computational approach to study 13 MOFs which were previously identified as the top adsorbents for CO₂/CH₄ and CO₂/N₂ separations in our previous work.¹⁷ AFEHUO, CIFCEB, FIRMUQ, KOSLUB, SUTBIT, and WONZIJ were studied as promising adsorbents for CO₂/CH₄ separation whereas AFEJOK, DATKIU, GUKYUI, HISJIE, LICCOQ, NIDBOS, and RIGVOU were examined for CO₂/N₂ separation. Structural properties of these MOFs such as PLD, the LCD, accessible gravimetric SA, PV, porosity (ϕ), and density (ρ) were computed using Zeo++ software.²⁹ For SA calculations, the trial number was set to 2000 and kinetic radius of N₂ was set to 1.86 Å. Probe radius was used as 0 Å and the trial number was set to 50,000 for geometric PV calculations. The MOFs that we studied in this work have a wide range of PLDs (4.3–9.8 Å), LCDs (5.4–11 Å), SAs (296.1–6069.8 m²/g) and PVs (0.2–1.4 cm³/g). These calculated properties together with the structural representations of 13 MOFs are given in Table S1 of the [Supporting Information](#).

GCMC simulations were used to study adsorption of CH₄, CO₂, H₂O, and N₂ in MOFs. All simulations were performed

with the Materials Studio 2017 (MS)³⁰ simulation package. Lennard-Jones 12-6 (LJ) and Coulomb potentials were used to model repulsion/dispersion forces and electrostatic interactions, respectively. The partial atomic charges of frameworks were estimated using the charge equilibration method (Qeq)³¹ as implemented in the MS to compute the electrostatic interactions between gas molecules and the atoms of frameworks. The electrostatic interactions were calculated by the Ewald summation with the accuracy of 0.001 kcal/mol.³² CO₂ was modeled as a three-site linear molecule with three LJ interactions sites located at each atom with partial point charges.³³ Similarly, N₂ was modeled as a three-site linear molecule with two sites located at two N atoms and the third one located at its center of mass with partial point charges.³⁴ Single-site spherical LJ 12-6 potential was used to model CH₄³⁵ molecules. The TIP4P/2005 water model³⁶ was used for H₂O molecules. Potential parameters used to describe the adsorbate molecules are given in Table S2. The potential parameters of MOFs were taken from the Universal force field (UFF)³⁷ and are given in Table S3. This force field was selected based on the results of previous simulation studies that showed the reliability of using UFF to compute CO₂, N₂, and CH₄ uptakes of MOFs.^{18,38} We note that we showed the good agreement between our molecular simulations and available experimental data for CO₂ uptakes, CO₂/N₂ selectivities, and CO₂/CH₄ selectivities of a large variety of MOFs in our previous work.¹⁷ The atom-based summation method with a cut-off radius of 13 Å for van der Waals terms was used. Simulation cell lengths were increased to at least 26 Å for each three dimensions. Periodic boundary conditions were applied in all simulations. MOFs were assumed to be rigid in their reported crystallographic structures to save significant computational time. For single-component GCMC simulations, three types of moves including translation, rotation, and regrowth of the molecule were used, whereas translation, exchange, rotation, and regrowth of the molecule were considered in mixture adsorption simulations. The Lorentz–Berthelot mixing rules were employed for pair-wise interactions. GCMC simulations were carried out for a total of 2 × 10⁶ steps with the first 10⁶ steps for equilibration and the last 10⁶ steps for production. More details about these simulation methods can be found in the literature.³⁹ Calculations were also performed using the sorption module of the MS for a total of 1 × 10⁷ production steps to compute Henry's constants of H₂O in MOFs and results are given in Table S4.

We focused on two different scenarios in this work: (i) binary (CO₂/CH₄ and CO₂/N₂) and ternary (CO₂/CH₄/H₂O and CO₂/N₂/H₂O) mixture adsorption simulations were performed using the fixed pressure task as implemented in the sorption module of the MS at 298 K at 0.1 and 1 bar. We note that slight differences in our previously reported CO₂ selectivities¹⁷ and the ones reported in this work can be attributed to the differences in the partial charges of MOF atoms assigned by the Qeq method. The original Qeq method³¹ which basically includes the electronegativity equalization was implemented in the MS, whereas a modified version of Qeq⁴⁰ that accounts for orbital interactions and uses an appropriate center for the Taylor series expansion in energy calculation as a function of the charges was implemented in the RASPA simulation code.⁴¹ We compared CO₂/CH₄ and CO₂/N₂ mixture adsorption results obtained from RASPA and MS in Figure S1 and we tabulated R² values for simulated gas uptakes using RASPA and MS in Table S5. As partial charges of frameworks affect the simulated gas uptakes in MOFs, we repeated the GCMC simulations by turning off the

electrostatic interactions between adsorbates and MOFs to isolate the effect of charge methods used in two simulation packages. As shown in Table S5, R² values for all gas uptakes were found to be >0.9 when only LJ interactions were considered, indicating that MS predicts almost the same gas uptake with RASPA.

The compositions of CO₂/CH₄ and CO₂/N₂ mixtures were set as 50/50 and 15/85, respectively. In order to keep the relative humidity of the system constant, the partial pressure of H₂O was kept at 0.0328 bar, which is 80% of the vapor pressure of the TIP4P H₂O model. For the CO₂/CH₄/H₂O mixture, the partial pressures of CO₂, CH₄, and H₂O were fixed at 0.0336/0.0336/0.0328 and 0.4836/0.4836/0.0328 bar for a total pressure of 0.1 and 1 bar, respectively. For the CO₂/N₂/H₂O mixture, the partial pressures of CO₂, N₂, and H₂O were fixed at 0.01008/0.05712/0.0328 and 0.14508/0.82212/0.0328 bar for a total pressure of 0.1 and 1 bar, respectively. (ii) For MOFs that are preloaded with H₂O before gas adsorption simulations, single-component H₂O adsorption isotherms were initially computed at 298 K up to 0.04 bar as shown in Figure S2. The number of adsorbed H₂O molecules that we computed at 0.025 bar, which corresponds to 80% relative humidity based on the equilibrium vapor pressure of H₂O at 298 K, was then loaded inside the MOFs using the fixed loading task as implemented in the sorption module of the MS and then binary gas adsorption simulations were performed using GCMC.

Results of molecular simulations were used to compute adsorbent performance evaluation metrics of MOFs, which are selectivity, working capacity, APS, and regenerability. Adsorption selectivities ($S_{\text{ads}(i/j)}$) of MOFs for separation of binary and ternary gas mixtures were calculated by eq 1 using the uptake (q) of gas species (i and j) in terms of mol/kg and their corresponding partial pressures (p_i and p_j) in terms of bar as follows

$$S_{\text{ads}(i/j)} = (q_i/q_j)/(p_i/p_j) \quad (1)$$

Working capacities (ΔN_i) of MOFs were calculated using the following equation

$$\Delta N_i = N_{\text{ads},i} - N_{\text{des},i} \quad (2)$$

where N_{ads} and N_{des} represent the uptake of the strongly adsorbed gas species i in terms of mol/kg computed at 1 bar (adsorption pressure) and 0.1 bar (desorption pressure), respectively. APS was computed as the product of selectivity and working capacity as follows⁴²

$$\text{APS} = S_{\text{ads}(i/j)} \times \Delta N_i \quad (3)$$

Regenerability ($R\%$), which is the per cent regeneration of the adsorption sites while desorption step is ongoing, is also an important adsorbent evaluation metric⁴³ and it was calculated using the following equation

$$R(\%) = (\Delta N_i/N_{\text{ads},i}) \times 100 \quad (4)$$

All adsorbent evaluation metrics defined above were calculated for CO₂ as it is more strongly adsorbed than CH₄ and N₂ in CO₂/CH₄ and CO₂/N₂ mixtures, respectively, in all MOFs.

3. RESULTS AND DISCUSSION

3.1. Comparing Simulation Results with Experiments.

Figure 1 shows the comparison of our simulation results with the experiments for single-component H₂O adsorption in different

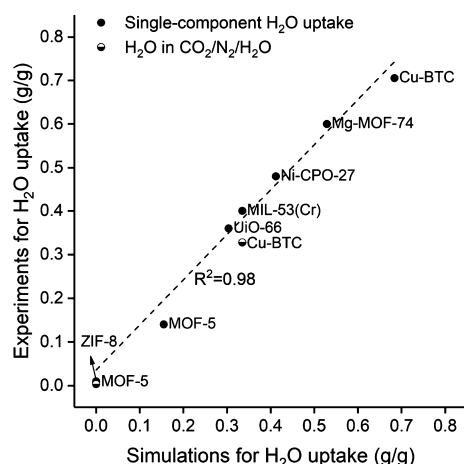


Figure 1. Comparison of our simulations with the experiments for single-component H₂O uptake in Cu-BTC,²¹ Mg-MOF-74,²⁴ MIL-53(Cr),²³ MOF-5,²² Ni-CPO-27,²⁵ UiO-66,²⁶ and ZIF-8²⁶ at 298 K and for multicomponent adsorption of H₂O in Cu-BTC²⁷ and MOF-5²⁷ at 313 K.

types of MOFs including Cu-BTC,²¹ MOF-5,²² MIL-53(Cr),²³ Mg-MOF-74,²⁴ Ni-CPO-27,²⁵ UiO-66,²⁶ and ZIF-8²⁶ at 298 K, and H₂O uptake in CO₂/N₂/H₂O mixture in Cu-BTC²⁷ and MOF-5²⁷ at 313 K. Details of experimental measurement conditions and our simulations are given in Table S6. Measurements for H₂O adsorption isotherms were reported as a function of P/P_0 that corresponds to the relative humidity at 298 K. Simulations were performed at the same conditions with experiments and the saturated H₂O uptakes were reported at 0.03 bar that corresponds to the saturated vapor pressure of H₂O

at 298 K. H₂O uptakes of MOF-5, Ni-CPO-27, and UiO-66 did not reach saturation at 0.03 bar; therefore, H₂O adsorption isotherms of these three MOFs were computed up to 0.1 bar. As shown in Figure 1, predictions of molecular simulations are in a good agreement with the experimentally reported data of both single-component H₂O adsorption and H₂O uptake in ternary CO₂/N₂/H₂O mixture in these MOFs. Simulations slightly underestimated single-component H₂O uptake in Mg-MOF-74, Ni-CPO-27, MIL-53(Cr), and UiO-66 at 298 K. For example, Schoenecker et al.²⁴ measured 0.62 g H₂O/g of Mg-MOF-74 at 298 K, 80% relative humidity, whereas we predicted H₂O uptake as 0.53 g/g at the same conditions. Canivet et al.²⁶ measured 0.36 g H₂O/g of UiO-66 at 298 K, 90% relative humidity and we computed the saturated H₂O uptake of UiO-66 as 0.30 g/g. It is important to note that slight deviations between simulations and experiments can be attributed to several reasons such as purity of structures, activation techniques, partial removal of solvent molecules, defects in crystal structures (experimental reasons), inadequacy of the potential models, and parameters used in molecular simulations (modeling reasons). Among these MOFs, Cu-BTC exhibited the highest H₂O uptake (~0.7 g/g) at 298 K.²⁴ On the other hand, a quite low H₂O uptake in MOF-5 (0.16 g/g) and negligible H₂O uptake in ZIF-8 (2.3×10^{-4} g/g) were calculated by our simulations which were also in a good agreement with experiments as shown in Figure 1. Multicomponent H₂O adsorption experiments are less common than the single-component H₂O adsorption experiments in the literature as it is difficult to accurately determine the composition and relative partial pressures of the gas phase at equilibrium.²⁷ We compared our simulation results with the experiments²⁷ for H₂O adsorption in the CO₂/N₂/H₂O mixture in MOF-5 and Cu-BTC at 313 K and as shown in Figure 1,

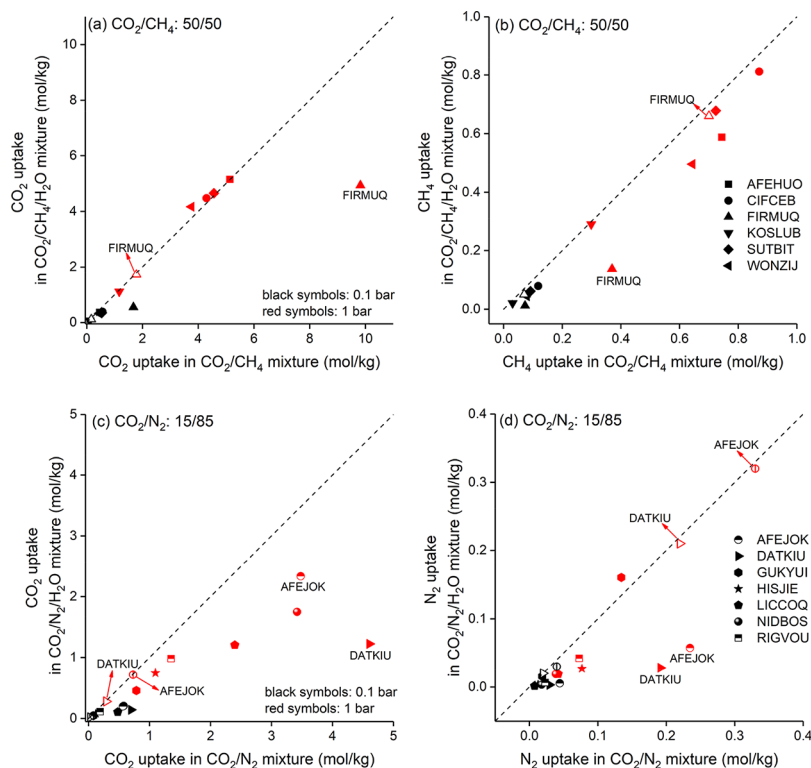


Figure 2. Comparison of (a) CO₂, (b) CH₄ uptakes in CO₂/CH₄ and CO₂/CH₄/H₂O mixtures, and (c) CO₂, (d) N₂ uptakes in CO₂/N₂ and CO₂/N₂/H₂O mixtures. Empty black and red symbols represent the gas uptake results for FIRMUQ, AFEJOK, and DATKIU obtained from simulations in which electrostatic interactions between the adsorbates–adsorbent were neglected at 0.1 and 1 bar, respectively.

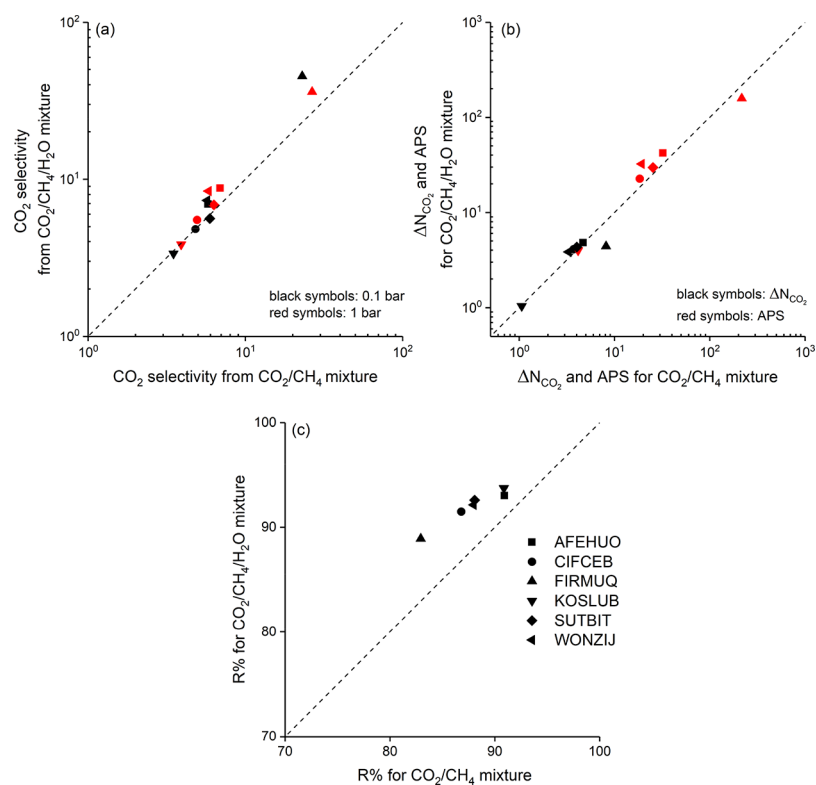


Figure 3. Comparison of (a) $S_{\text{CO}_2/\text{CH}_4}$, (b) ΔN_{CO_2} (mol/kg) and APS (mol/kg), (c) R % of MOFs calculated for separation of CO₂/CH₄ and CO₂/CH₄/H₂O mixtures.

simulations agreed well with the experiments for both Cu-BTC and MOF-5. Overall, these comparisons showed that molecular simulations can be used to accurately estimate both the single-component and multicomponent adsorption of H₂O in MOFs.

3.2. Effect of H₂O on CO₂/CH₄ and CO₂/N₂ Separation Performances of MOFs. H₂O vapor can dramatically change the CO₂ uptake in MOF adsorbents because of the competition of gas molecules with the H₂O molecules for the same adsorption sites of materials. Therefore, it is important to examine the impact of H₂O on the natural gas and flue gas separation performances of the best MOF candidates. We focused on AFEHUO, CIFCEB, FIRMUQ, KOSLUB, SUTBIT, and WONZIJ, which were identified as the top candidates for CO₂/CH₄ separation, and AFEJOK, DATKIU, GUKYUI, HISJIE, LICCOQ, NIDBOS, and RIGVOU, which were identified as the top materials for CO₂/N₂ separation in our previous work where we also showed the good agreement between simulated CO₂ selectivities and available experimental data of some of these promising MOFs.¹⁷ GCMC simulations were performed for these 13 MOFs at 0.1 and 1 bar, 298 K to compute the adsorption of CO₂/CH₄: 50/50 and CO₂/N₂: 15/85 mixtures. In order to show how the presence of H₂O affects the adsorption of CO₂, CH₄, and N₂ in MOFs, we compared binary mixture (CO₂/CH₄ and CO₂/N₂) adsorption data with the ternary mixture (CO₂/CH₄/H₂O and CO₂/N₂/H₂O) adsorption data in Figure 2. Figure 2a shows that CO₂ uptakes of MOFs except for FIRMUQ do not dramatically change when H₂O was introduced as the ternary component into CO₂/CH₄ mixture at 0.1 and 1 bar. For FIRMUQ, CO₂ uptake significantly decreased from 9.82 to 4.93 mol/kg at 1 bar when H₂O was present in the mixture. This decrease can be attributed to the competition between H₂O and CO₂ molecules for the fluorine-functionalized adsorption sites of the framework, which have a

strong affinity toward guest molecules because of the electrostatic interactions with the adsorbates. Similar results were also observed in the literature⁴⁴ for fluorinated porous organic frameworks. Introduction of the fluorine groups in frameworks enhanced CO₂ adsorption compared to their nonfluorinated counterparts because of the increase of the heat of adsorption for CO₂ driven by the strong electrostatic interactions among C–F dipoles. In order to unlock the impact of the electrostatic interactions between CO₂ molecules and the fluorine-functionalized adsorption sites of FIRMUQ, we switched off the electrostatic interactions between the adsorbate molecules and adsorbent in molecular simulations and recomputed the gas uptakes. As shown in Figure 2a, CO₂ uptake in the binary CO₂/CH₄ mixture (1.78 mol/kg) and CO₂ uptake in the ternary CO₂/CH₄/H₂O mixture (1.72 mol/kg) were found to be almost the same at 1 bar. This indicates that in the absence of electrostatic interactions between adsorbates and adsorbent, H₂O has almost no effect on the CO₂ uptake of FIRMUQ. On the other hand, when the electrostatic interactions were considered in molecular simulations, co-adsorption of H₂O significantly reduced the CO₂ uptake capacity of FIRMUQ.

Figure 2b shows the change in CH₄ uptakes of MOFs in the presence of H₂O in the CO₂/CH₄ mixture. CH₄ uptakes of CIFCEB, KOSLUB, and SUTBIT slightly decreased in the presence of H₂O, whereas the decreases were more pronounced for AFEHUO, FIRMUQ, and WONZIJ. For example, CH₄ uptake of WONZIJ decreased from 0.64 to 0.50 mol/kg at 1 bar. Similarly, in the presence of H₂O, CH₄ uptake of FIRMUQ (AFEHUO) decreased from 0.37 to 0.14 mol/kg (0.74–0.59 mol/kg) at 1 bar. These three MOFs, AFEHUO, FIRMUQ, and WONZIJ, have fluorine-functionalized adsorption sites, which enhance guest affinities of the frameworks because of the strong electrostatic interactions with the adsorbate molecules as we

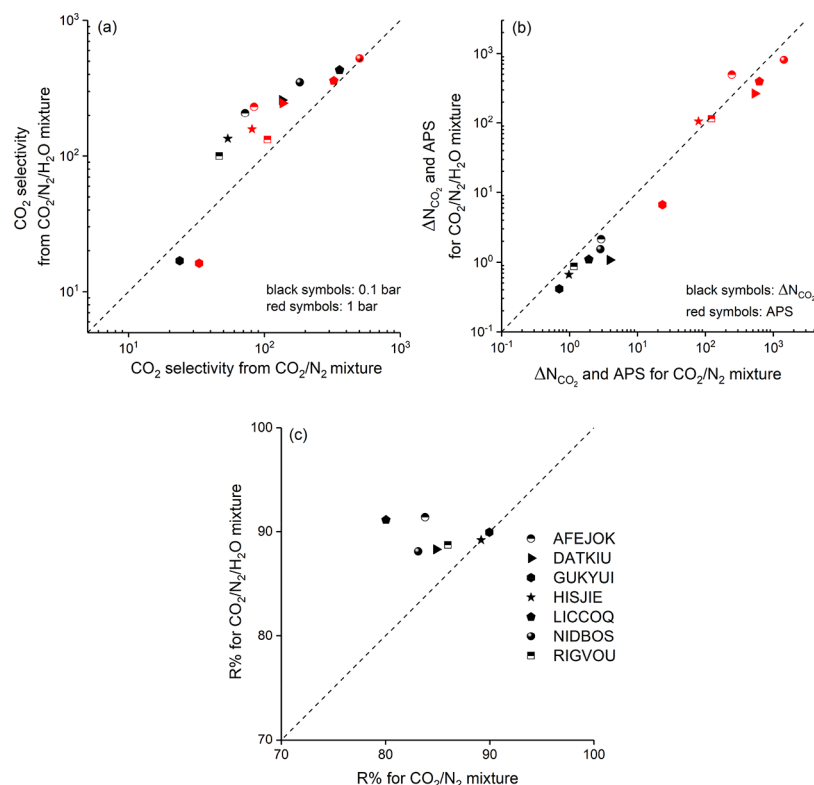


Figure 4. Comparison of (a) $S_{\text{CO}_2/\text{N}_2}$, (b) ΔN_{CO_2} (mol/kg) and APS (mol/kg), (c) R % of MOFs calculated for separation of CO₂/N₂ and CO₂/N₂/H₂O mixtures.

discussed above. When the electrostatic interactions between adsorbates and FIRMUQ were neglected in simulations, CH₄ uptakes of FIRMUQ in the CO₂/CH₄ mixture (0.07 and 0.70 mol/kg at 0.1 and 1 bar, respectively) and those in the CO₂/CH₄/H₂O mixture (0.05 and 0.66 mol/kg at 0.1 and 1 bar, respectively) were found to be similar. This result indicates that co-adsorption of H₂O has no effect on CH₄ uptake of FIRMUQ when the electrostatic interactions are omitted. Overall, results revealed that the presence of H₂O in the gas mixture has a strong impact on the gas uptakes of MOFs having fluorine-functional groups.

A comparison of Figure 2a,c represents that the presence of H₂O in the CO₂/N₂ mixture has a more pronounced effect on the CO₂ adsorption compared to the presence of H₂O in the CO₂/CH₄ mixture. Especially for AFEJOK, DATKIU, LICCOQ, and NIDBOS, CO₂ uptake significantly decreased in the presence of H₂O at 1 bar as shown in Figure 2c. Similarly, N₂ uptake in AFEJOK and DATKIU significantly decreased in the presence of H₂O as shown in Figure 2d. The decreases in CO₂ and N₂ uptakes in these MOFs can be attributed to the presence of extra framework anions including hexafluorophosphates (PF₆⁻) and tetrafluoroborates (BF₄⁻), which enhance the electrostatic interactions between adsorbates and MOFs in these structures. We observed that Cu atoms of AFEJOK that are bonded to PF₆⁻ have high partial charges (+4.06 e⁻), which enhance the electrostatic interactions between CO₂-MOF and N₂-MOF. When the adsorbate-adsorbent electrostatic interactions were switched off for AFEJOK and DATKIU, CO₂ and N₂ uptakes did not significantly change at 0.1 and 1 bar in the presence of H₂O as shown in Figure 2c,d. For example, when the adsorbate-adsorbent electrostatic interactions were neglected in binary and ternary mixture adsorption simulations, CO₂ (N₂)

uptake in DATKIU very slightly decreased from 0.29 (0.22) to 0.28 (0.21) mol/kg in the presence of H₂O vapor at 1 bar. Similar to DATKIU, CO₂ (N₂) uptake in AFEJOK slightly decreased from 0.73 (0.33) to 0.72 (0.32) mol/kg in the presence of H₂O at 1 bar. It is also important to note that H₂O uptake of these MOFs in the CO₂/N₂/H₂O mixture remarkably decreased when the adsorbate-MOF electrostatic interactions were omitted. For example, if the adsorbent-adsorbate electrostatic interactions were neglected in simulations, H₂O uptake of DATKIU in the CO₂/N₂/H₂O mixture significantly decreased from 15.53 to 0.01 mol/kg at 1 bar. Therefore, we can conclude that strong adsorption of H₂O molecules within the pores of AFEJOK and DATKIU is mainly driven by the electrostatic interactions.

We so far examined the effect of H₂O on the gas uptakes of MOFs and now turn to the impact of H₂O on the calculated adsorbent performance evaluation metrics of MOFs such as CO₂ selectivity, CO₂ working capacity, APS, and R %. The results obtained from the ternary CO₂/CH₄/H₂O mixture simulations were compared with those obtained from binary CO₂/CH₄ mixture simulations in Figure 3. CO₂ uptakes of all MOFs except FIRMUQ increased in the presence of H₂O at 1 bar, whereas CH₄ uptakes of all MOFs decreased at the same condition as we discussed above. This leads to increased CO₂ selectivities for all MOFs except KOSLUB at 1 bar as shown in Figure 3a. Both CO₂ and CH₄ uptakes of KOSLUB slightly decreased, resulting in an almost unchanged CO₂ selectivity at 1 bar. CO₂ selectivities of FIRMUQ and WONZIJ computed for the CO₂/CH₄/H₂O mixture at 1 bar were 35 and 44% higher than that those computed for the binary CO₂/CH₄ mixture, respectively. The increase in the selectivity of WONZIJ was because of the increase in CO₂ uptake in the presence of H₂O at

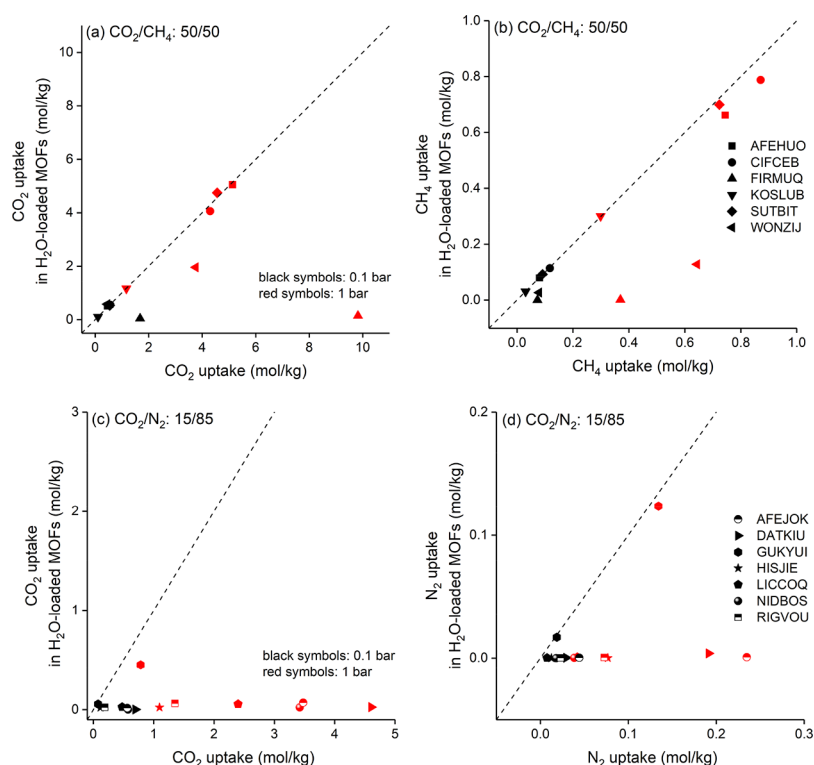


Figure 5. Comparison of (a) CO_2 , (b) CH_4 uptakes in pristine MOFs and H_2O -loaded MOFs and (c) CO_2 , (b) N_2 uptakes in pristine MOFs and H_2O -loaded MOFs for the CO_2/N_2 mixture.

1 bar. On the other hand, the increase in CO_2 selectivity of FIRMUQ in the presence of H_2O can be explained by the higher rate of decrease in CH_4 uptake compared to the decrease in CO_2 uptake. As shown in Figure 3b, CO_2 working capacities and APS values of all MOFs except FIRMUQ increased in the presence of H_2O . Similarly, R % of all MOFs increased in the presence of H_2O in Figure 3c because of the increase in CO_2 working capacities. Although CO_2 working capacity and CO_2 uptake of FIRMUQ decreased at 1 bar, its regenerability increased because of the increase in the ratio of working capacity to CO_2 uptake.

Figure 4 shows the change in adsorbent performance evaluation metrics of AFEJOK, DATKIU, GUKYUI, HISJIE, LICCOQ, NIDBOS, and RIGVOU for CO_2/N_2 separations in the presence of H_2O . There are significant changes in the predicted CO_2/N_2 separation performances of MOFs in the presence of H_2O . A comparison of Figures 3 and 4 presents that CO_2 selectivities, working capacities, APSs, and R % values computed for CO_2/N_2 mixtures were much more affected by the presence of H_2O than those calculated for CO_2/CH_4 mixtures. As shown in Figure 4a, CO_2 selectivities computed for the ternary $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ mixture were much higher than those calculated for the binary CO_2/N_2 mixture except for GUKYUI. The most remarkable increases in CO_2 selectivities were observed for AFEJOK (almost tripled in the presence of H_2O) and DATKIU (almost doubled in the presence of H_2O). The numbers of adsorbed H_2O molecules in these two MOFs were significantly higher than those observed in the rest of the MOFs both at 0.1 and 1 bar. For example, H_2O uptake of AFEJOK (DATKIU) in the $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ mixture was calculated as 7.24 (15.53) mol/kg at 1 bar, whereas H_2O uptake of the rest of the MOFs in the $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ mixture was calculated as ~ 3 mol/kg at 1 bar. The H_2O affinity of AFEJOK and DATKIU can be

attributed to the presence of nonbonded fluorine-containing anions (PF_6^- and BF_4^-) in their frameworks. In order to support the strong H_2O affinity of AFEJOK and DATKIU, we also calculated Henry's constants of H_2O in MOFs as listed in Table S4. Henry's constants of H_2O in AFEJOK (6.9×10^2 mmol/g/bar) and DATKIU (1.5×10^5 mmol/g/bar) were found to be much higher than that of ZIF-8 (2.7×10^{-1} mmol/g/bar), which was reported as a hydrophobic MOF in the literature because of its low Henry's constant.⁴⁵ Snapshots taken from the GCMC simulations of AFEJOK and DATKIU with the adsorbed CO_2 , N_2 , and H_2O molecules at 1 bar, 298 K, are given in Figure S3. Nonbonded fluorine-containing anions of both AFEJOK and DATKIU were surrounded with CO_2 molecules in the adsorption simulations of the binary CO_2/N_2 mixture. When H_2O was introduced into the gas mixture, these sites were primarily surrounded by the H_2O molecules. Because of the strong affinity toward H_2O and the competition between H_2O molecules and other adsorbates, the number of adsorbed N_2 molecules in these MOFs dramatically decreased, resulting in higher CO_2 selectivities in the ternary mixture separation. As shown in Figure 4b, CO_2 working capacities (APSs) of all (most) MOFs decreased in the presence of H_2O . Similar to CO_2/CH_4 separation, R % of all MOFs studied for CO_2/N_2 separation increased in the presence of H_2O as shown in Figure 4c. Overall, the presence of H_2O as the third component in the flue gas mixture significantly affects the predicted adsorbent performance evaluation metrics of MOFs, which have high Henry's constants of H_2O . This result hints that computing Henry's constants of H_2O in MOFs can be a useful initial screening strategy to quantify the H_2O affinity of MOFs before performing GCMC simulations to compute adsorption of flue gas mixture.

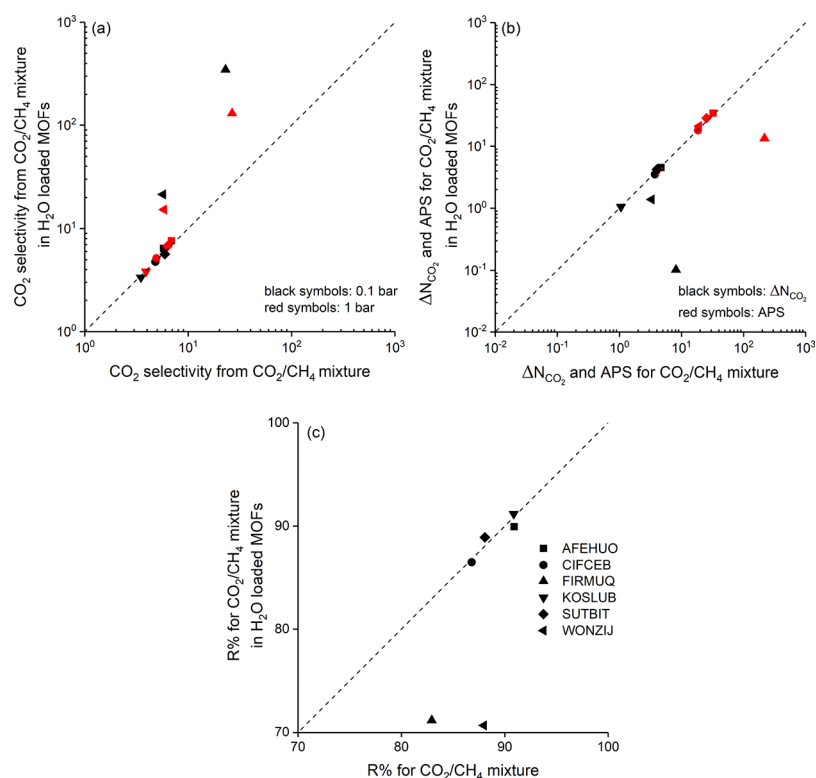


Figure 6. Comparison of (a) $S_{\text{CO}_2/\text{CH}_4}$, (b) ΔN_{CO_2} (mol/kg) and APS (mol/kg), (c) R % of H_2O -loaded MOFs and pristine MOFs.

3.3. Effect of Preadsorbed H_2O on CO_2/CH_4 and CO_2/N_2 Separation Performances of MOFs. In order to mimic experimental measurements in which H_2O is first injected into the adsorbent and then gas molecules are injected with increasing pressure, we computed CO_2/CH_4 and CO_2/N_2 mixture uptakes in H_2O -loaded MOFs. Adsorbed H_2O loadings were computed at 0.025 bar corresponding to 80% of the vapor pressure of H_2O from the single-component H_2O adsorption isotherms of MOFs as shown in Figure S2. Type I isotherm is dominant for adsorption of H_2O in these MOFs and the more rectangular type I saturated H_2O adsorption isotherms of FIRMUQ, DATKIU, and AFEJOK can be attributed to the strong adsorption of H_2O molecules at low pressures because of the favorable fluorine-functionalized adsorption sites of these MOFs as we discussed above. Similar adsorption isotherm types were also discussed in the literature for zeolites 5A and 13X, which have calcium and sodium cations providing strong adsorption sites for H_2O molecules.⁴⁶

Figure 5 compares CO_2 , CH_4 , and N_2 uptakes of pristine MOFs with those of MOFs that were preloaded with H_2O at 298 K. Figure 5a demonstrates that CO_2 uptake in H_2O -loaded MOFs, AFEHUO, CIFCEB, KOSLUB, and SUTBIT, was found to be almost the same with their unloaded counterparts. This can be attributed to low H_2O uptakes of these MOFs at 0.025 bar as shown in Figure S2. As FIRMUQ has a strong affinity toward H_2O , which was also supported by high Henry's constant of H_2O (7.5×10^7 mmol/g/bar), CO_2 uptake in this MOF dramatically decreased from 9.82 to 0.14 mol/kg at 1 bar when the framework was preloaded with H_2O . We provided the average adsorbed H_2O density maps taken from the snapshots of GCMC simulations of FIRMUQ in Figure S4 at 0.005 and 0.04 bar. Even at very low pressures such as 0.005 bar, the most favorable adsorption sites of FIRMUQ were occupied by the H_2O molecules and when the pressure was increased to 0.04 bar,

energetically less favorable adsorption sites became available. Furthermore, the decrease in the adsorbed H_2O density was clearly observed in Figure S4 when the framework charges were omitted in molecular simulations resulting in low H_2O uptake in FIRMUQ as we discussed before. Figure 5b shows that except for FIRMUQ and WONZIJ, CH_4 uptakes in pre- H_2O -loaded MOFs were found to be almost the same with those in pristine MOFs.

The top MOF adsorbents identified for CO_2/N_2 separation exhibited stronger H_2O affinity than those identified for CO_2/CH_4 separation. As shown in Table S4, Henry's constants of H_2O of the MOFs studied for CO_2/CH_4 separation were found to be much lower than those of the MOFs studied for CO_2/N_2 separation. Therefore, the number of adsorbed H_2O molecules in AFEJOK, DATKIU, GUKYUI, HISJIE, LICCOQ, NIDBOS, and RIGVOU was computed to be much higher than that of AFEHUO, CIFCEB, KOSLUB, and SUTBIT at 0.025 bar. Because of the high number of adsorbed H_2O molecules, both CO_2 and N_2 uptakes significantly decreased in the H_2O -loaded MOFs as shown in Figure 5c,d. For example, when H_2O molecules were loaded into DATKIU, simulated CO_2 (N_2) uptake of this MOF drastically dropped to 0.03 ($\sim 4 \times 10^{-3}$) mol/kg at 1 bar, compared to the corresponding gas uptake in pristine MOF, 4.61 (0.19) mol/kg. Similarly, simulated CO_2 (N_2) uptake of AFEJOK significantly decreased to 0.07 ($\sim 8 \times 10^{-4}$) mol/kg at 1 bar, compared to the corresponding gas uptake in pristine AFEJOK, 3.48 (0.23) mol/kg. Because of the high adsorbed number of H_2O molecules in AFEJOK (15.8 mol/kg) and DATKIU (22.6 mol/kg) at 0.025 bar, CO_2 and N_2 molecules could not find enough space for adsorption, resulting in significant decreases in CO_2 and N_2 uptakes of these MOFs.

We then computed selectivity, working capacity, APS, and R % of pre- H_2O -loaded MOFs for both CO_2/CH_4 and CO_2/N_2 separations. Figure 6a shows that CO_2 selectivities of MOFs,

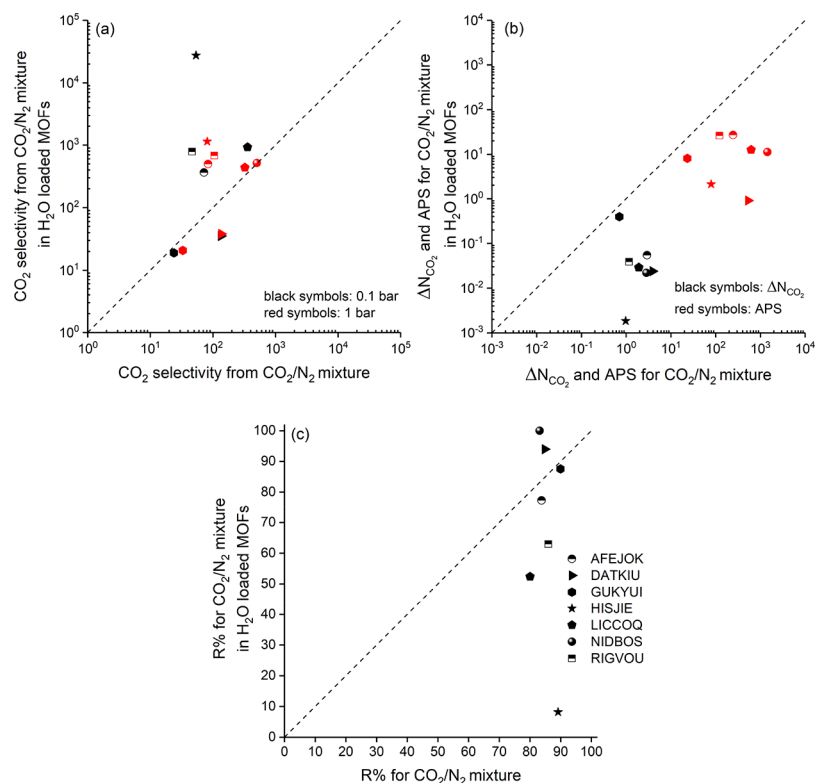


Figure 7. Comparison of (a) $S_{\text{CO}_2/\text{N}_2}$, (b) ΔN_{CO_2} (mol/kg) and APS (mol/kg), (c) R % of H₂O-loaded MOFs and pristine MOFs.

except FIRMUQ and WONZIJ, did not change as both CO₂ and CH₄ uptakes decreased in H₂O-loaded MOFs. Similarly, CO₂ working capacity, APS, and R % values of AFEHUO, CIFCEB, KOSLUB, and SUTBIT were almost the same for pristine MOFs and H₂O-loaded MOFs as shown in Figure 6b,c. As these MOFs have weak affinities toward H₂O, the number of adsorbed H₂O molecules was calculated to be low, resulting in an almost negligible effect on the CO₂, CH₄ uptakes and calculated adsorbent performance evaluation metrics of MOFs. The weak H₂O affinities of these MOFs were also supported by Henry's constants we computed for H₂O as given in Table S4. KOSLUB and SUTBIT can be considered as hydrophobic materials because of their negligible H₂O uptakes (~0.07 mol/kg) at 0.025 bar and their low Henry's constants of H₂O (2.4 mmol/g/bar and 8.9×10^{-1} mmol/g/bar for KOSLUB and SUTBIT, respectively). CO₂ selectivities of FIRMUQ and WONZIJ significantly increased (Figure 6a) although their CO₂ working capacities decreased (Figure 6b). This was attributed to negligible CH₄ uptakes in these MOFs. As the CO₂ working capacity of FIRMUQ considerably decreased compared to that of WONZIJ as shown in Figure 6b, the APS value of FIRMUQ, which was calculated as the multiplication of the CO₂ working capacity by CO₂ selectivity at 1 bar decreased. On the other hand, the increase in CO₂ selectivity and the decrease in CO₂ working capacity of WONZIJ compensated each other and resulted in almost an unchanged APS. It is important to note that calculated R % values dropped below 80% for both FIRMUQ and WONZIJ as shown in Figure 6c as both CO₂ working capacities and CO₂ uptakes of these MOFs remarkably decreased compared to those of their pristine counterparts. Considering the fact that R % is an important criterion in screening of MOF adsorbents to eliminate the ones having R % <85%, our results revealed that exposure of an MOF adsorbent

to H₂O prior to CO₂/CH₄ should be carefully considered in the material selection process.

Figure 7 shows how the predicted CO₂/N₂ separation performances of MOFs change in the presence of different H₂O loadings in the frameworks. CO₂ selectivities of AFEJOK, HISJIE, LICCOQ, NIDBOS, and RIGVOU increased, whereas CO₂ selectivities of DATKIU and GUKYUI decreased at 1 bar when pre-H₂O-loaded MOFs were considered in binary CO₂/N₂ mixture adsorption simulations as shown in Figure 7a. The increase in CO₂ selectivity of HISJIE at both pressures was quite remarkable. N₂ uptake in this MOF dramatically decreased when H₂O-loaded HISJIE was used; therefore, CO₂ selectivity of H₂O-loaded HISJIE was calculated to be very high. Similarly, both CO₂ and N₂ uptakes significantly decreased when H₂O was loaded into NIDBOS. As the CO₂ uptake of NIDBOS at 0.1 bar was found to be almost zero, we could not report its CO₂ selectivity at that pressure in Figure 7a. It is important to note that both HISJIE and NIDBOS have low PVs (0.31 and 0.36 cm³/g, respectively) and low accessible SAs (361.15 and 539.12 m²/g, respectively). Because of the high H₂O loadings, N₂ molecules could not be adsorbed in these MOFs. Figure 7b shows that both CO₂ working capacities and APSs of MOFs decreased in the pre-H₂O-loaded case for CO₂/N₂ separation. The decrease in CO₂ working capacities significantly affected R % predictions as shown in Figure 7c. R % values of only DATKIU and NIDBOS increased in the H₂O-loaded case, which can be attributed to their negligible CO₂ uptakes at 0.1 bar. Overall, results so far revealed that exposure of MOFs to H₂O prior to gas adsorption significantly alter selectivity, working capacity, regenerability of the promising MOFs for CO₂/N₂ separation, whereas the presence of H₂O within the frameworks was found to have a less pronounced effect on the predicted CO₂/CH₄ separation performances of the promising MOFs.

The promising MOF adsorbents are generally selected based on the combination of APS and R % values as we discussed in our previous works.^{17,47,48} We showed that the presence of H₂O in the feed gas mixture or preloading of H₂O into the MOF may significantly alter the calculated APS and R % values of the top-performing MOFs in some cases. As identification of the top material candidates strongly depends on these metrics, we computed the coefficient of determination (R^2) for all metrics for (i) binary and ternary mixture separations and (ii) pristine and H₂O-loaded MOFs for binary mixture separations. Values of R^2 are listed in Table 1. For the CO₂/CH₄ mixture, R^2 values for

Table 1. Calculated R^2 for the Adsorbent Performance Evaluation Metrics of MOFs

	CO ₂ /CH ₄ separation		CO ₂ /N ₂ separation	
	binary vs ternary mixture separation	pristine MOFs vs H ₂ O-loaded MOFs	binary vs ternary mixture separation	pristine MOFs vs H ₂ O-loaded MOFs
S at 0.1 bar	0.996	0.987	0.852	0.067
S at 1 bar	0.996	0.987	0.889	0.001
APS	0.984	0.034	0.788	0.016
ΔN_{CO_2}	0.505	0.031	0.461	0.219
R %	0.945	0.504	0.077	0.056

CO₂ selectivities were found to be almost 1, indicating that separation performances of the top MOFs based on CO₂ selectivities are not strongly affected by the presence of H₂O. Similarly, R^2 values for APS and R % were high, 0.98 and 0.95, respectively, indicating that results of binary CO₂/CH₄ mixture adsorption simulations can be used to predict adsorbent performances of MOFs for ternary CO₂/CH₄/H₂O mixtures. However, R^2 value for ΔN_{CO_2} was found to be low, 0.51, because of the remarkable changes in CO₂ uptakes of FIRMUQ in the presence of H₂O. When FIRMUQ was neglected in the analysis, the R^2 value increased from 0.51 to 0.98, suggesting that results of binary CO₂/CH₄ mixture adsorption simulations can be also used to predict ΔN_{CO_2} of MOFs for ternary CO₂/CH₄/H₂O separation if MOFs do not have specific functional groups showing high affinity for H₂O. For CO₂/N₂ separation, R^2 values for CO₂ selectivities and APS were found to be high (>0.85 and 0.79, respectively). However, R^2 values for ΔN_{CO_2} and R % were low, 0.46 and 0.08, respectively. The very low R^2 value for R % was attributed to the remarkable increases in the R % values of LICCOQ (~14%) and AFEJOK (~9%) when a ternary CO₂/N₂/H₂O mixture was considered. An important message of these results is that adsorbent performance evaluation metrics of promising MOFs identified for CO₂/CH₄ separation exhibit less sensitivity to the presence of H₂O in the gas mixture than those of promising MOFs identified for CO₂/N₂ separations. When H₂O was preloaded in MOFs prior to binary mixture GCMC simulations, calculated R^2 values for all metrics as shown in Table 1 were found to be very low, indicating that there is a weak correlation between the results obtained for pristine MOF and those obtained for H₂O-loaded MOFs. For example, selectivity did not significantly change but both APS and R % of H₂O-loaded MOFs were found to be very different than those calculated for pristine MOFs for CO₂/CH₄ separation, resulting in lower R^2 values. In the case of CO₂/N₂ separations, the calculated R^2 values for pristine and H₂O-loaded MOFs were very low, showing the impact of the presence of H₂O in the

framework on the separation performances of MOFs. We finally note that the number of top-performing MOFs studied in this work is quite low; hence, R^2 values may change if a high number of materials is considered.

We so far solely focused on the effect of H₂O on the gas separation performances of the top MOFs. Choosing an efficient adsorbent which is stable under humid conditions is important for practical CO₂ capture applications. The H₂O stability of a small number of MOFs such as Cu-BTC and ZIF-8 was reported in the literature.⁴⁹ We examined the experimental synthesis papers of the MOFs we considered in this work and found information about the H₂O stability of two MOFs. KOSLUB⁵⁰ and SUTBIT⁵¹ were reported to be H₂O-stable. Liu et al.²⁵ showed that Ni/DOBDC, the structural isomer of KOSLUB, can maintain its CO₂ uptake capacity after multiple exposures to H₂O vapor, consistent with our results. SUTBIT was also reported to have a moisture-insensitive nature and very high thermal stability.⁵¹ Further experimental studies are required to assess the CO₂ separation performances of the rest of promising MOFs under humid conditions.

Finally, it is important to note that an approximate partial charge assignment method and a generic force field were used in this work. We recently showed that adsorbent performance evaluation metrics of MOFs such as selectivities computed for CO₂/CH₄ and CO₂/N₂ separation using Qeq and DDEC (the density-derived electrostatic and chemical) charges were similar.¹⁷ The role of partial charge assignment methods on CO₂ capture under humid conditions was previously discussed in the literature. For example, Li et al.¹⁸ observed that the difference between EQeq (the extended charge equilibration) and REPEAT (the repeating electrostatic potential extracted atomic) charges is small for Henry's constants of N₂ and CO₂, whereas Henry's constant of H₂O was found to be more sensitive to the partial charge assignment method. They reported that the EQeq method underestimates the interaction strength between H₂O and MOF atoms, resulting in high CO₂/H₂O selectivities. The ranking of the top 15 MOFs based on their CO₂/H₂O selectivities was found to be almost insensitive to the partial charge assignment method. Li et al.¹⁹ reported that 8 out of the top 15 MOFs identified from computational screening of MOFs using DDEC and EQeq charges based on the ratios of Henry's constant of CO₂ and H₂O were identical. Performing more detailed quantum chemistry calculations in future studies would be very useful to accurately describe the electrostatic interactions between CO₂, N₂, and H₂O molecules and the frameworks considering a large number of diverse MOF structures.

4. CONCLUSIONS

Performing molecular simulations for adsorption of CO₂/CH₄/H₂O and CO₂/N₂/H₂O mixtures for several thousands of MOFs is computationally very demanding because of the very low acceptance ratios for insertions and deletions of H₂O molecules in the GCMC simulations. In this work, we examined the effects of the presence of H₂O in the natural gas and flue gas mixtures on the predicted adsorbent evaluation metrics of the top promising MOF adsorbents that were previously identified as the best adsorbents among 54808 MOFs. CO₂ selectivity, CO₂ working capacity, APS, and R % of the top-performing MOFs were computed considering adsorption of ternary CO₂/CH₄/H₂O and CO₂/N₂/H₂O mixtures and compared with those computed considering adsorption of binary CO₂/CH₄ and CO₂/N₂ mixtures. The results showed that introduction of H₂O

as the third component in CO₂/CH₄ and CO₂/N₂ mixtures significantly affected the adsorbent evaluation metrics of the top promising MOF adsorbents that have strong affinity toward H₂O because of the presence of specific functional groups and/or extra framework anions. As the MOFs identified as promising for CO₂/N₂ separation exhibited stronger H₂O affinity than those identified for CO₂/CH₄ separation, CO₂ separation performance metrics computed for those MOFs were much more affected by the presence of H₂O. Our molecular simulations on H₂O pre-loaded MOFs showed that exposure of an MOF to H₂O prior to gas adsorption can cause drastic decreases in their calculated CO₂ working capacities, APSs, and R % for CO₂/N₂ separation. The presence of H₂O within the pores of MOFs prior to adsorption increased their CO₂/N₂ selectivities. Overall, results of this work will be highly useful to guide the future studies on the design and development of new MOF adsorbents that can achieve high-performance CO₂ separations under humidity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.9b05487>.

Comparison of CO₂, CH₄, and N₂ uptakes of MOFs obtained from GCMC simulations for CO₂/CH₄: 50/50 and CO₂/N₂: 15/85 mixtures at 298 K using RASPA and MS; single-component H₂O adsorption isotherms of 13 MOFs; GCMC snapshots of AFEJOK and DATKIU with adsorbed CO₂, N₂, and H₂O molecules; average H₂O density maps for FIRMUQ obtained from single-component GCMC simulations; structural properties of the top 13 MOF adsorbents together with their chemical formula; potential parameters used to describe CH₄, CO₂, N₂, and H₂O; UFF parameters used in molecular simulations; Henry constants (mmol/g/bar) of H₂O in MOFs; calculated R² for CO₂, CH₄, and N₂ uptakes of 13 MOFs obtained from mixture GCMC simulations at 298 K using RASPA and MS; and conditions for experimental and simulated single-component and mixture H₂O uptake data of MOFs shown in Figure 1 (PDF)

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Notes

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■ REFERENCES

- (1) Li, C.; Meckler, S. M.; Smith, Z. P.; Bachman, J. E.; Maserati, L.; Long, J. R.; Helms, B. A. Engineered Transport in Microporous Materials and Membranes for Clean Energy Technologies. *Adv. Mater.* **2018**, *30*, 1704953–1704986.
- (2) Xian, S.; Peng, J.; Zhang, Z.; Xia, Q.; Wang, H.; Li, Z. Highly Enhanced and Weakened Adsorption Properties of Two MOFs by Water Vapor for Separation of CO₂/CH₄ and CO₂/N₂ Binary Mixtures. *Chem. Eng. J.* **2015**, *270*, 385–392.
- (3) Herm, Z. R.; Krishna, R.; Long, J. R. CO₂/CH₄, CH₄/H₂ and CO₂/CH₄/H₂ Separations at High Pressures Using Mg₂ (dobdc). *Microporous Mesoporous Mater.* **2012**, *151*, 481–487.
- (4) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. Selective Gas Adsorption and Separation in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- (5) Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. Progress in Adsorption-based CO₂ Capture by Metal-Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 2308–2322.
- (6) Li, B.; Wen, H.-M.; Zhou, W.; Chen, B. Porous Metal-Organic Frameworks for Gas Storage and Separation: What, How, and Why? *J. Phys. Chem. Lett.* **2014**, *5*, 3468–3479.
- (7) Sabouni, R.; Kazemian, H.; Rohani, S. Carbon Dioxide Capturing Technologies: A Review Focusing on Metal Organic Framework Materials (MOFs). *Environ. Sci. Pollut. Res.* **2014**, *21*, 5427–5449.
- (8) Yu, J.; Xie, L.-H.; Li, J.-R.; Ma, Y.; Seminario, J. M.; Balbuena, P. B. CO₂ Capture and Separations Using MOFs: Computational and Experimental Studies. *Chem. Rev.* **2017**, *117*, 9674–9754.
- (9) Bacsik, Z.; Cheung, O.; Vasiliev, P.; Hedin, N. Selective Separation of CO₂ and CH₄ for Biogas Upgrading on Zeolite NaKA and SAPO-56. *Appl. Energy* **2016**, *162*, 613–621.
- (10) Allen, F. H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380–388.
- (11) Watanabe, T.; Sholl, D. S. Accelerating Applications of Metal-Organic Frameworks for Gas Adsorption and Separation by Computational Screening of Materials. *Langmuir* **2012**, *28*, 14114–14128.
- (12) Wilmer, C. E.; Farha, O. K.; Bae, Y.-S.; Hupp, J. T.; Snurr, R. Q. Structure-Property Relationships of Porous Materials for Carbon Dioxide Separation and Capture. *Energy Environ. Sci.* **2012**, *5*, 9849–9856.
- (13) Aghaji, M. Z.; Fernandez, M.; Boyd, P. G.; Daff, T. D.; Woo, T. K. Quantitative Structure-Property Relationship Models for Recognizing Metal Organic Frameworks (MOFs) with High CO₂ Working Capacity and CO₂/CH₄ Selectivity for Methane Purification. *Eur. J. Inorg. Chem.* **2016**, 4505–4511.
- (14) Lin, L.-C.; Berger, A. H.; Martin, R. L.; Kim, J.; Swisher, J. A.; Jariwala, K.; Rycroft, C. H.; Bhowan, A. S.; Deem, M. W.; Haranczyk, M.; Smit, B. In silico screening of carbon-capture materials. *Nat. Mater.* **2012**, *11*, 633–641.
- (15) Qiao, Z.; Zhang, K.; Jiang, J. In Silico Screening of 4764 Computation-Ready, Experimental Metal-Organic Frameworks for CO₂ Separation. *J. Mater. Chem. A* **2016**, *4*, 2105–2114.
- (16) Chung, Y. G.; Camp, J.; Haranczyk, M.; Sikora, B. J.; Bury, W.; Krungleviciute, V.; Yildirim, T.; Farha, O. K.; Sholl, D. S.; Snurr, R. Q. Computation-Ready, Experimental Metal-Organic Frameworks: A Tool to Enable High-Throughput Screening of Nanoporous Crystals. *Chem. Mater.* **2014**, *26*, 6185–6192.
- (17) Altintas, C.; Avci, G.; Daglar, H.; Nemati Vesali Azar, A.; Velioglu, S.; Erucar, I.; Keskin, S. Database for CO₂ Separation Performances of MOFs Based on Computational Materials Screening. *ACS Appl. Mater. Interfaces* **2018**, *10*, 17257–17268.
- (18) Li, S.; Chung, Y. G.; Snurr, R. Q. High-throughput Screening of Metal-Organic Frameworks for CO₂ Capture in the Presence of Water. *Langmuir* **2016**, *32*, 10368–10376.
- (19) Li, W.; Rao, Z.; Chung, Y. G.; Li, S. The Role of Partial Atomic Charge Assignment Methods on the Computational Screening of

Metal-Organic Frameworks for CO₂ Capture under Humid Conditions. *ChemistrySelect* **2017**, *2*, 9458–9465.

(20) Coelho, J. A.; Lima, A. E. O.; Rodrigues, A. E.; de Azevedo, D. C. S.; Lucena, S. M. P. Computer Simulation of Adsorption and Siting of CO₂, N₂, CH₄ and Water on a New Al(OH)-Fumarate MOF. *Adsorption* **2017**, *23*, 423–431.

(21) Liang, Z.; Marshall, M.; Chaffee, A. L. CO₂ Adsorption-based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X). *Energy Fuels* **2009**, *23*, 2785–2789.

(22) Ming, Y.; Purewal, J.; Yang, J.; Xu, C.; Soltis, R.; Warner, J.; Veenstra, M.; Gaab, M.; Müller, U.; Siegel, D. J. Kinetic Stability of MOF-5 in Humid Environments: Impact of Powder Densification, Humidity Level, and Exposure Time. *Langmuir* **2015**, *31*, 4988–4995.

(23) Bourrelly, S.; Moulin, B.; Rivera, A.; Maurin, G.; Devautour-Vinot, S.; Serre, C.; Devic, T.; Horcajada, P.; Vimont, A.; Clet, G.; Daturi, M.; Lavalley, J.-C.; Loera-Serna, S.; Denoyel, R.; Llewellyn, P. L.; Férey, G. Explanation of the Adsorption of Polar Vapors in the Highly Flexible Metal Organic Framework MIL-53(Cr). *J. Am. Chem. Soc.* **2010**, *132*, 9488–9498.

(24) Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S. Effect of Water Adsorption on Retention of Structure and Surface Area of Metal-Organic Frameworks. *Ind. Eng. Chem. Res.* **2012**, *51*, 6513–6519.

(25) Liu, J.; Wang, Y.; Benin, A. I.; Jakubczak, P.; Willis, R. R.; LeVan, M. D. CO₂/H₂O Adsorption Equilibrium and Rates on Metal-Organic Frameworks: HKUST-1 and Ni/DOBDC. *Langmuir* **2010**, *26*, 14301–14307.

(26) Canivet, J.; Bonnefoy, J.; Daniel, C.; Legrand, A.; Coasne, B.; Farrusseng, D. Structure-Property Relationships of Water Adsorption in Metal-Organic Frameworks. *New J. Chem.* **2014**, *38*, 3102–3111.

(27) Mason, J. A.; McDonald, T. M.; Bae, T.-H.; Bachman, J. E.; Sumida, K.; Dutton, J. J.; Kaye, S. S.; Long, J. R. Application of a High-Throughput Analyzer in Evaluating Solid Adsorbents for Post-Combustion Carbon Capture via Multicomponent Adsorption of CO₂, N₂, and H₂O. *J. Am. Chem. Soc.* **2015**, *137*, 4787–4803.

(28) Moghadam, P. Z.; Li, A.; Wiggin, S. B.; Tao, A.; Maloney, A. G. P.; Wood, P. A.; Ward, S. C.; Fairen-Jimenez, D. Development of a Cambridge Structural Database Subset: A Collection of Metal-Organic Frameworks for Past, Present, and Future. *Chem. Mater.* **2017**, *29*, 2618–2625.

(29) Willems, T. F.; Rycroft, C. H.; Kazi, M.; Meza, J. C.; Haranczyk, M. Algorithms and Tools for High-Throughput Geometry-Based Analysis of Crystalline Porous Materials. *Microporous Mesoporous Mater.* **2012**, *149*, 134–141.

(30) Dassault Systèmes BIOVIA. *BIOVIA Pipeline Pilot*; Dassault Systèmes: San Diego, B. W., Release 2017.

(31) Rappe, A. K.; Goddard, W. A., III Charge Equilibration for Molecular Dynamics Simulations. *J. Phys. Chem.* **1991**, *95*, 3358–3363.

(32) Ewald, P. P. Die Berechnung Optischer und Elektrostatistischer Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.

(33) Potoff, J. J.; Siepmann, J. I. Vapor-Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. *AIChE J.* **2001**, *47*, 1676–1682.

(34) Makrodimitris, K.; Papadopoulos, G. K.; Theodorou, D. N. Prediction of Permeation Properties of CO₂ and N₂ through Silicalite via Molecular Simulations. *J. Phys. Chem. B* **2001**, *105*, 777–788.

(35) Martin, M. G.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. 1. United-Atom Description of N-Alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577.

(36) Abascal, J. L. F.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505–234517.

(37) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

(38) McDaniel, J. G.; Li, S.; Tyljanakis, E.; Snurr, R. Q.; Schmidt, J. R. Evaluation of Force Field Performance for High-Throughput Screening

of Gas Uptake in Metal-Organic Frameworks. *J. Phys. Chem. C* **2015**, *119*, 3143–3152.

(39) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Academic Press, 2001.

(40) Wilmer, C. E.; Snurr, R. Q. Towards Rapid Computational Screening of Metal-Organic Frameworks for Carbon Dioxide Capture: Calculation of Framework Charges via Charge Equilibration. *Chem. Eng. J.* **2011**, *171*, 775–781.

(41) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: Molecular Simulation Software for Adsorption and Diffusion in Flexible Nanoporous Materials. *Mol. Simul.* **2016**, *42*, 81–101.

(42) Chung, Y. G.; Gomez-Gualdrón, D. A.; Li, P.; Leperi, K. T.; Deria, P.; Zhang, H. D.; Vermeulen, N. A.; Stoddart, J. F.; You, F. Q.; Hupp, J. T.; Farha, O. K.; Snurr, R. Q. In Silico Discovery of Metal-Organic Frameworks for Precombustion CO₂ Capture Using a Genetic Algorithm. *Sci. Adv.* **2016**, *2*, No. e1600909.

(43) Bae, Y.-S.; Snurr, R. Q. Development and Evaluation of Porous Materials for Carbon Dioxide Separation and Capture. *Angew. Chem., Int. Ed.* **2011**, *50*, 11586–11596.

(44) Comotti, A.; Castiglioni, F.; Bracco, S.; Perego, J.; Pedrini, A.; Negroni, M.; Sozzani, P. Fluorinated Porous Organic Frameworks for Improved CO₂ and CH₄ Capture. *Chem. Commun.* **2019**, *55*, 8999–9002.

(45) Qiao, Z.; Xu, Q.; Jiang, J. Computational Screening of Hydrophobic Metal-Organic Frameworks for the Separation of H₂S and CO₂ from Natural Gas. *J. Mater. Chem. A* **2018**, *6*, 18898–18905.

(46) Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S. Effect of Water Adsorption on Retention of Structure and Surface Area of Metal-Organic Frameworks. *Ind. Eng. Chem. Res.* **2012**, *51*, 6513–6519.

(47) Altintas, C.; Erucar, I.; Keskin, S. High-throughput Computational Screening of the Metal Organic Framework Fatabase for CH₄/H₂ Separations. *ACS Appl. Mater. Interfaces* **2018**, *10*, 3668–3679.

(48) Avci, G.; Velioğlu, S.; Keskin, S. High-throughput Screening of MOF Adsorbents and Membranes for H₂ Purification and CO₂ Capture. *ACS Appl. Mater. Interfaces* **2018**, *10*, 33693–33706.

(49) Burtch, N. C.; Jasuja, H.; Walton, K. S. Water Stability and Adsorption in Metal-Organic Frameworks. *Chem. Rev.* **2014**, *114*, 10575–10612.

(50) Kapelewski, M. T.; Geier, S. J.; Hudson, M. R.; Stück, D.; Mason, J. A.; Nelson, J. N.; Xiao, D. J.; Hulvey, Z.; Gilmour, E.; FitzGerald, S. A.; Head-Gordon, M.; Brown, C. M.; Long, J. R. M₂(m-dobdc) (M = Mg, Mn, Fe, Co, Ni) Metal-Organic Frameworks Exhibiting Increased Charge Density and Enhanced H₂ Binding at the Open Metal Sites. *J. Am. Chem. Soc.* **2014**, *136*, 12119–12129.

(51) Galli, S.; Masciocchi, N.; Colombo, V.; Maspero, A.; Palmisano, G.; López-Garzón, F. J.; Domingo-García, M.; Fernández-Morales, I.; Barea, E.; Navarro, J. A. R. Adsorption of Harmful Organic Vapors by Flexible Hydrophobic Bis-Pyrazolate based MOFs. *Chem. Mater.* **2010**, *22*, 1664–1672.