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Molecular dynamic simulations of hydrophilic MIL-160-based membrane demonstrate pressure-dependent selective uptake of industrially relevant greenhouse gases†

Jordan Chapman a, Nagasree Garapati a, Vassiliki-Alexandra Glezakou b, Yuhua Duan c, Jianli Hu a, Cerasela Zoica Dinu a

The continued integration of technologies capable of achieving higher degrees of sustainability while meeting global material and energy demands is of singular importance in halting human-caused climate change. Unit operations of gas separations membranes composed of metal-organic frameworks (MOFs) are considered promising candidates for such integration, owing to their modular, scalable nature and high degree of tunability required to maintain separation functionality. However, prior to sustainable implementation, both an evaluation of MOF characteristics and an intensive examination of MOF-gas molecule interactions are necessary to fully understand the fundamental separation criteria, as well as to define suitable ranges of gas separations conditions. Herein, we present our findings on the greenhouse gas separations capabilities of the hydrophilic, Al-based MIL-160 in the selective uptake of carbon dioxide (CO₂) from other relevant greenhouse gases, i.e., methane (CH₄), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), and nitric oxide (NO), including gravimetric solubility, permeability, and diffusivity calculations. We found that a MIL-160 membrane has excellent applicability in the separation of gases with varying electronegativities, noting diffusivity selectivities of 72.0, 9.53, and 13.8 for CH₄, NO₂, and NO, respectively, relative to CO₂. Further, we demonstrate that the selectivity at which gas molecules diffuse through the MIL-160 membrane varies strongly with the simulation pressure, suggesting that MIL-160 is a potentially ideal candidate for the development of pressure-swing adsorption processes that perform gas separations efficiently while mitigating emissions of greenhouse gases.

Introduction

The societal need for efficient, scalable gas separation processes has become of great significance following the enactment of international agreements that aim simultaneously to decelerate anthropogenic emissions and to implement an increased share of sustainably designed energy technologies1-8. The separation of acid gases carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from natural gas resources, for instance, is an important precursor to the improved economics downstream emissions. Complementarily, the separation of flue gas impurities such as sulfur (SO₂), nitrogen oxides (NOₓ), and other trace gases offers a general platform for mitigating the hydrolytic formation of acids in the presence of water thus subsequently improving process affordability and sustainability1, 4, 11. Lastly, post combustion separation of CO₂ from dilute low flow rate stream aids in the industrialization and efficiency of chemical processes with specific trade-offs in capture rates12. Whereas the storage and transportation of CO₂ are facilitated by relatively mature, affordable technologies13-15, CO₂ capture—including its separation from other gases—continues to prove challenging and comprises nearly 66% of the total costs associated with carbon capture and storage (CCS) processes5-7, 16-19.

A number of gas adsorption and separation technologies that operate on the basis of differences in gas physical properties—i.e., volatility, solubility, adsorptivity, and molecular diameters of the individual gases, respectively—have been developed and implemented at the commercial scale, with varying degrees of applicability in the selective uptake of target greenhouse gases1, 2, 20-22 however with drawbacks. Specifically, distillation columns, absorbers, and strippers often entail considerable heat requirements and are either infeasible for the separation of incondensable gases or incur significant operating costs associated with the purchase of chemical solvents and maintenance of optimized operating conditions for instance1. 2, 23. Further, such technologies require relatively large capital investment for well-defined process specifications and thus are profitable only when the scale of production is

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a West Virginia University, Morgantown, WV 26506, United States
b Pacific Northwest National Laboratory, Richland, WA 99352, United States
c National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, Pennsylvania 15236, United States
large enough with respect to both the time of operation and materials’ lifetime.

Pressure swing adsorption (PSA) was recently exploited for the removal of vapor-phase impurities and enrichment of usable gases benefitting from low energy input and facile implementation at varied production scale. Similarly, gas separations via microporous polymer membranes have been commercially employed for the oxygen enrichment of air, recovery of hydrogen from ammonia production process streams, and the upgrade of natural gas. Still, challenges persist when considering gas drying, fractionation of air, off-gases scalability and the ensuing difficulty of bringing bench-scale findings to consumer scale implementation. Moreover, porous polymer membranes suffer from critical tradeoffs between permeability and gas molecule selectivity thus resulting in low efficiency of separations due to inconsistent pore size distributions and low gas selectivity.

Metal-organic frameworks (MOFs)—porous materials with high specific surface areas, controllable nanostructures, and tunable chemical and physical properties—have recently been proposed as alternatives for CCS processes and for gas adsorption and separation. The modular nature of MOFs with aperture size distributions of angstrom-level resolution is envisioned to allow for high degrees of adsorption selectivity and permeability and improved process economics with reduced emissions. Previous studies showed that a mixed-matrix membrane (MMM) composed of a polyimide crosslinker and embedded with NH$_2$-MIL-53, a surface-modified variant of an aluminum-based MOF, can be used for separating CH$_4$ from CO$_2$—exhibiting increased CO$_2$ selectivity without significant loss of its permeability. The improvements were realized in part by the presence of NH$_2$ groups that aided in regulating the MOF breathing mechanism and penetration of polyimide chains to provide configurational stability. Complementary, a new humidity-resistant MOF, JNU-2 has shown promise in separation of ethane (C$_2$H$_6$) from ethylene (C$_2$H$_4$), the single largest feedstock in the petrochemicals industry. The efficiency of the separation was bolstered by the combination of the rational design of the JNU-2 aperture sites and its high availability in surface area. These authors and others showed that optimal MOF performance is often focused on the combined synergistic effects resulting from dynamic structural, chemical, mechanical, and electrical properties of such hybrids. However, it was also found that a significant portion of current MOFs were highly unstable in the presence of moisture in adsorption/separation processes; for instance, isoreticular metal-organic frameworks (IRMOFs) lost their porosity at room temperature in air thus considerably reducing process efficiency. Similarly, some classes of carboxylated MOF materials exhibit significant structural variations in neutral to basic media due to the deprotonation of the water molecules coordinated to the metal nodes within the MOF, thus leading to a cascade of reactions with subsequent loss of native pore geometry.

Herein, we hypothesized that intrinsic MOF characteristics—including selective affinity for target gas molecules, desired operability across varied temperatures and pressures, highly regular and controllable pore geometry, and structural stability in aqueous environments—will ultimately determine the MOF’s feasibility for implementation in membrane systems to be used for gas separation processes. Furthermore, we hypothesized that the inherent chemical stability of such MOFs in solvents and caustic gases that can otherwise cause inhibitory loss of framework native pore structure and, by extension, loss of MOF performance, will expand the applicability of such materials to a widening range of end uses.

To demonstrate our hypotheses, we used a hydrophilic MOF, MIL-160, known for its high hydrothermal stability and selective and reversible adsorption of water vapor. MIL-160 is readily synthesized via chemically mild conditions and was shown to have large potential applicability for gas sorption and refrigeration technologies, respectively. For instance, Permyakova et al., were successful in synthesizing up to 400 g per day of Al-based MIL-160 via the equimolar mixture of aluminum acetate and 2,5-furandicarboxylic acid in 2 L of water at room temperature followed by an ethanol wash and drying at 100 °C; the product was implemented as a water sorbent in a heat reallocation open-system reactor that outperformed the commercial zeolite thirteen times in seasonal heat storage showing good promise of MIL-160-based sorbents in energy reallocation systems with a water capacity of nearly 0.36 g water g$^{-1}$ MIL-160 and full regeneration of water at 80 °C. Solovyeva et al., reported synthesis by mixing in equimolar amounts 2,5-furandicarboxylic acid, aluminum chloride hexahydrate, and sodium hydroxide, all in distilled water heating the product at 120 °C prior to washing it and activating it via continuous evacuation at 150 °C for 15 h. Synthesized MIL-160 was implemented in an atmospheric water harvesting scheme in which the binding affinity for water and the hydrothermal stability of the MOF material distinguished it as an ideal candidate with specific water capacity of nearly 0.34 g water g$^{-1}$ MIL-160 and a regeneration temperature of 80 °C. Lastly, in our lab we have shown synthesis of MIL-160-alumina based membranes as supports for CO$_2$ capture and transformation in benign byproducts upon interfacing of the framework with carbonic anhydrase enzyme.

Brandt et al., have further confirmed the promising potential of MIL-160 in gas separation processes owing to its high selectivity for SO$_2$ at low partial pressures, as well as its excellent stability in both humid and dry conditions. Moreover, Wu et al., developed a MIL-160 based membrane prepared on polydopamine-modified aluminum oxide discs via a solvothermal synthesis route that was implemented in the separation of p-xylene from its bulkier isomer o-xylene; the membrane was found to have a separation factor of 38.5—competitive with zeolitic metal-inorganic framework counterparts—owing to high diffusion and adsorption selectivities of p-xylene relative to o-xylene. However, to our knowledge, no studies exist that directly relate the dynamic sorption behavior of different greenhouse gas species within a MIL-160 membrane or to the steady-state permeability and adsorptivity of such species. Moreover, we found no analyses that correlate the variations in chemical and physical MOF-gas molecule interactions direct the suitability of MIL-160 for gas...
separation application. Lack of such knowledge presents not only an apparent gap in performance analysis of this specific MOF but further prevents future improvements strategies of applicability to other MOFs structures and their integration in gas adsorption and separation processes.\textsuperscript{2, 22, 31, 32}

Methodology

General considerations for MD simulations.

Atomic-level processes critical to MOF membrane efficiency— including pressure-driven selective adsorption and selective permeability of industrially relevant gas species CO\textsubscript{2}, CH\textsubscript{4}, sulfur dioxide (SO\textsubscript{2}), nitrogen dioxide (NO\textsubscript{2}), and nitric oxide (NO)—were investigated for the selected framework aluminum (Al)-based MIL-160, constructed from the coordination of 2,5-furandicarboxylic acid with Al ions.\textsuperscript{46} All molecular dynamics (MD) simulations were performed using GROMACS software version 2016.\textsuperscript{69} Non-bonded force field parameters of MIL-160 including partial atomic charges derived via single point energy calculations and Mulliken analysis were taken from Cadiau et al.\textsuperscript{30}; the structure of MIL-160 was assumed to be rigid such that the atomic coordinates of MIL-160 were fixed. Transferable potentials for phase equilibria (TraPPE) parameters for CO\textsubscript{2}, SO\textsubscript{2}, NO\textsubscript{3}, NO,\textsubscript{54}, and CH\textsubscript{4}\textsubscript{55} were used to define both the Lenard-Jones and electrostatic interactions between the MOF membrane and gas molecules.

Membrane simulations.

The membrane was simulated via construction of a MOF supercell with increased numbers of unit cells in all dimensions; the process was chosen to reflect controlled scaling within the limits of computational budget. All simulations were run in the canonical NVT ensemble (constant number of molecules, volume, and temperature, respectively) and at 300 K; simulation temperature was maintained via the V-rescale thermostat algorithm.\textsuperscript{56} Van der Waals (VDW) interactions between atoms were measured at a cut-off range of 1.4 nm for sufficient sampling of gas particle-MOF interactions without burdensome computational expense, while long range electrostatics were calculated with a Particle Mesh Ewald (PME) scheme for the elimination of potential electrostatic artifacts. Time integration of the simulations was done following the leap-frog integration method.\textsuperscript{58} Simulation boxes with dimensions of 8.4 nm x 8.4 nm determined by the dimension of the 4 x 4 MIL-160 membrane and varying dimensions in the z-direction depending on the target simulation pressure were constructed; a 4 x 4 x 3 MIL-160 membrane was placed in each box such that a gas bath was placed on one side of the membrane while the other side of the membrane remained a vacuum chamber, thus creating an effective pressure gradient that varied in magnitude with the number of gas molecules contained in respective gas baths. A schematic representation of the simulation scenario is shown in Fig. S.1 in Supporting Info.

Membrane permeation and sorption characteristics.

To evaluate membrane permeation and sorption characteristics of individual gas species, single-component gas baths—e.g., 100 mol\% CO\textsubscript{2}, 100 mol\% CH\textsubscript{4}, 100 mol\% SO\textsubscript{2}, 100 mol\% NO\textsubscript{2}, 100 mol\% NO—were inserted on one side of the MIL-160 membrane, thus emulating a physical scenario consistent with typical pressure-driven membrane processes. Gas mixtures comprised of 95 mol\% CH\textsubscript{4}/5 mol\% CO\textsubscript{2}, 95 mol\% SO\textsubscript{2}/5 mol\% CO\textsubscript{2}, 95 mol\% NO\textsubscript{2}/5 mol\% CO\textsubscript{2}, and 95 mol\% NO/5 mol\% CO\textsubscript{2} were similarly placed on one side of the MIL-160 membrane opposite a vacuum chamber to determine the dilute CO\textsubscript{2} separation capabilities of the MOF membrane relative to the chemical and physical properties of respective gas molecules. Pressure of each gas bath was varied from vacuum conditions to high-pressure conditions—0.2, 0.5, 1, 5, 50 bar—by changing the number of molecules contained within the gas bath to calculate pressure-dependent sorption and permeation characteristics of the MIL-160 membrane. Simulation pressure was varied across a wide range spanning vacuum, atmospheric, and high-pressure regimes to thus survey broadly the atomic level phenomena that endow a MIL-160 membrane with its critical separation criteria even for applications related to carbon sequestration with enhanced gas recovery.\textsuperscript{60}

Gas bath pressures were calculated following the assumption that each gas did not deviate from ideal behaviour. Tables S.1 and S.2 in Supporting Information summarize the number of gas molecules, molar composition, simulation box dimensions, and effective simulation pressure of each single-composition gas simulation and gas mixture simulation, respectively. It is noted that the simulation size of high-pressure simulations run at gas bath pressure 50 bar were decreased relative to all other simulations in order to avoid severely limiting computational expenses associated with a large number of atoms within the simulations.

Initial configurations were energy-minimized via the steepest descent method at a time step of 1 fs prior to a timestep of 1 fs for 100-ps intervals, after which gas baths containing a depleted number of gas molecules owing to pressure-driven sorption and permeation were replaced with gas baths comprised of the same number and molar composition as the initial gas bath, whereas gas molecules that had permeated to the vacuum chamber were removed. Thus, temporal decreases in gas bath pressure were accounted for at each 100-ps interval and corrected via the replacement of a depleted gas bath with a gas bath containing the appropriate number of molecules pertaining to the desired gas bath pressure and molar composition. Replacement of depleted gas baths and removal of permeated gas molecules at 100-ps intervals were necessary to account for gas molecules that either were adsorbed within the membrane or permeated through the membrane into the vacuum chamber and, therefore, were needed to approximate constant pressure gradients while running sequential MD productions in the canonical NVT ensemble.\textsuperscript{60}

An energy minimization in which the gas molecule atomic positions were optimized via the steepest descent method to
prevent energetically prohibitive placement was run following the introduction of the gas baths at each 100-ps interval. Following energy minimization, sequential 100-ps simulations were run, and deplated gas baths were again replaced to adjust for pressure deviations. This process was extended for total data collection periods ranging from 10 ns to 120 ns simulation time as was necessary to capture both dynamic and steady-state sorption and permeation behaviors of each gas species at varied gas bath pressures. The numbers of adsorbed and permeated gas molecules were measured via a molecule-counting shell script in which gas molecules located within the MOF membranes were defined as adsorbed gas molecules and gas molecules that migrated to the vacuum side of the simulation were defined as permeated gas molecules.

The permeability \( P_s \), gravimetric solubility \( S_s \), and diffusivity \( D_s \) of each gas species were calculated from the single-component gas simulations, using Equations 1-3:\(^{60}\)

\[
P_s = \frac{N_p}{A l} \\
S_s = \frac{m}{\rho S} \\
D_s = \frac{N_p}{\Delta t}
\]

where \( N_p \) represents the number of permeated molecules, \( N_p \) is the Avogadro’s number, \( l \) is the length of the MIL-160 membrane in the z-direction, \( A \) is the area of the MIL-160 membrane in the xy-plane, \( p_i \) represents the partial pressure of gas molecules for species i in the gas bath, \( \Delta t \) the time period in which \( N_p \) molecules permeated, \( m \), the mass of gas molecules within the MIL-160 membrane, and \( m_{MOF} \) is the mass of the MIL-160 membrane, respectively.

Complementary, the permselectivity \( \alpha_{P,i} \), gravimetric solubility selectivity \( \alpha_{S,i} \), and diffusivity selectivity\(^{60} \( \alpha_{D,i} \)) of CH\(_4\), SO\(_2\), NO\(_2\), and NO relative to CO\(_2\) were calculated according to Equations 4-6:

\[
\alpha_{P,i} = \frac{P_i}{P_{CO_2}} \\
\alpha_{S,i} = \frac{S_i}{S_{CO_2}} \\
\alpha_{D,i} = \frac{D_i}{D_{CO_2}}
\]

where \( P_s, S_s \), and \( D_s \) are calculated as defined above in Equations 1-3 for gas species CH\(_4\), SO\(_2\), NO\(_2\), and NO and \( P_{CO_2}, S_{CO_2}, D_{CO_2} \) are calculated for gas species CO\(_2\).

Statistical analysis.

Statistical analysis was conducted for single-component calculations and gas mixture selectivity calculations. The average number of adsorbed gas molecules as well as the average number of permeated gas molecules was calculated for each single-component gas simulation at steady-state sorption and permeation regimes. Further, standard deviations around the average numbers of adsorbed gas molecules and permeated gas molecules were calculated for the same conditions.

Similar analysis with slight adjustments in the approach was carried out for gas mixture simulations. Averages were calculated for the ratio of adsorbed gas molecules CH\(_4\), SO\(_2\), NO\(_2\), and NO to adsorbed CO\(_2\) molecules as well as the permeated gas molecules CH\(_4\), SO\(_2\), NO\(_2\), and NO to permeated CO\(_2\) molecules, all respectively, at steady-state sorption and permeation regimes. Standard deviations around the average ratios of adsorbed gas molecules and average ratios of permeated gas molecules were calculated as well.

Results and discussion

Membrane permeation and sorption of single-component gases.

We first conducted MD simulations emulating steady-state permeation of various gases—i.e., CO\(_2\), CH\(_4\), SO\(_2\), NO\(_2\), NO—through a rigid MIL-160 membrane at pressures 0.2, 0.5, 1, 5, and 50 bar, respectively, to probe permeability and sorption characteristics through MIL-160 defined membranes. Herein, we define steady-state conditions as those in which the number of gas molecules within the MIL-160 membrane and the rate of gas molecules permeating through the membrane approach respective constant values dependent on gas bath pressure and gas species properties. The gases were chosen because they are known to cause significant logistical problems within chemical refineries and power plants leading to catalyst poisoning and evolution of corrosive species that were shown to damage equipment as well as contribute to the acceleration of human-caused climate change.\(^{10,61,62}\) For our analysis, we implemented reliable force field parameters for both gas molecules and membrane systems to thus circumvent the computational constraints of density functional theory (DFT) methods\(^{63}\) known to be computationally expensive and often prohibitive in supplementing key thermodynamic findings like energy optimized configurations of adsorbed guest molecules with permeabilities resulting from the energetic preferability with which a MOF material binds target gas molecules.\(^{60,64}\)

Figure 1 shows the sorption, permeability, and diffusivity of each single-component gas composition were calculated with respect to a rigid 4 x 4 x 3 MIL-160 membrane (Figure 1(a)). The dynamic sorption and permeation profiles of simulated gas species at each pressure are presented in Supporting Information Figures S.2-S.6. Our analysis showed that each tested gas species followed a time-dependent trend in which the sorption of an individual molecule within the membrane reached a saturation point, i.e., the maximum loading, with the permeation rates approaching a constant rate within a simulation time to depend on the employed simulation pressure. High-pressure simulations reached steady-state conditions in less time than did simulations running in vacuum and atmospheric conditions respectively. Gas permeation analysis at 5 bar and 50 bar elicited dynamic responses within 10 ns of simulation time, while atmospheric and vacuum condition required simulation times up to 120 ns to reach steady-state sorption and permeation behaviors.

Analysis also showed that gravimetric solubility and the rate at which individual gas molecules permeated through the
defined MOF membrane varied significantly with respect to the simulation pressure as well as across the simulated gas species respectively. This was presumably due to differences in chemical and physical properties among the gas molecules tested with results showing that MIL-160 membrane possessed higher loading capacity for oxygenated gas species relative to non-oxygenated species, at all pressures sampled. CH$_4$ had a lower gravimetric solubility in the MIL-160 membrane than did the oxygen-containing gas species in both high-pressure and low-pressure regimes (Figure 1(b)). The trend in gravimetric solubility of oxygenated gas species showed a strong dependence on simulation pressure, while the solubility of CH$_4$ varied significantly only at high pressures.

The above are presumably due to the hydrophilic nature of MIL-160 and the electrostatic interactions of the gases with the membrane, respectively. First, the hydrophilic nature of the MOF can contribute to favorable interactions with the electronegative regions of the studied gas molecules to provide thermodynamically preferred configurations in which the oxygenated gas molecules can stably adsorb within the membrane structure itself$^{65}$. Second, the electrostatic interactions are expected to play an active role in establishing critical separation criteria for potential processes employing MIL-160-based membranes$^{60}$. In particular, we found that a MIL-160 membrane has strong potential to separate to an appreciable degree gas molecules of different electronegativities, owing to stark differences in the preferability with which MIL-160 binds highly electronegative gas molecules like SO$_2$ and CO$_2$ over less electronegative molecules like CH$_4$ and NO at varied pressure regimes.

The general decrease in gravimetric solubility at higher pressures coincided with maximized gas molecule loadings within MIL-160, i.e., an increase in pressure did not seem to increase the number of molecules within the membrane and thus drove the gravimetric solubility downward. Our analysis also showed that both the abundance of polar surface area of each gas molecule and the electronegativity of the oxygen atoms in the respective molecules impacted their gravimetric solubility. Moreover, the increase in oxygen atom electronegativity coincided with increased gravimetric solubilities of the simulated species. Specifically, the increased electronegativity of the oxygen atoms in SO$_2$ relative to those in CO$_2$, NO$_2$, and NO molecules, respectively, was expected to lead to higher molecular packing in the membrane by driving the equilibrium distance between MIL-160 and the adsorbed gas molecules downward such that a greater portion of the native MOF cage structure being preserved during the adsorption process$^{40}$. Such preservation is expected to allow for effective gas permeation at high- and low-pressure regimes, while loss of native MOF cage structure due to high gas molecule packing is seen as inhibitory to gas molecule permeation. Similarly, we found that the simulation pressure influenced the permeability of oxygenated gas species through the MIL-160 membrane to varying extents again, dependent on interactions between gas molecules themselves and the membrane. The permeability of CH$_4$ however did not change considerably with varied

![Fig 1.](image-url) (a) MIL-160 (i) unit cell extended dimensionally to generate (ii) MOF membrane applied in gas separation simulations; (b) gravimetric solubility, (c) permeability, and (d) diffusivity of selected gas molecules sampled at varied pressures relative to a rigid 4 x 4 x 3 MIL-160 membrane.
simulation pressure most likely due to the absence of strong interactions with the MIL-160 membrane.

Figure 1(c) illustrates the variations in permeabilities of each gas molecule evaluated in our study and across high- and low-pressure regimes respectively. Our analysis showed that the relationship between simulation pressure and the gas molecule permeability is subject to complex tradeoffs between MOF-gas molecule interactions and associated thermodynamic barriers pertaining to desorption processes itself. In particular, the pressures at which oxygenated gas species exhibited significant increases in permeability was influenced by the strength of the interactions between the respective gas molecule and the MIL-160 membrane. For instance, NO showed an increase in permeability starting at 0.5 bar possibly because low pressures were sufficient to partially overcome thermodynamic barriers in the desorption of the molecule from the MIL-160 membrane. The subsequent decrease in permeability at pressures of 5 bar and higher was likely due to diminishing increases in the number of molecules permeated. Meanwhile, SO$_2$ had a gravimetric solubility nearly 9 times that of NO at 0.5 bar—calculated via Equation 2 and shown in Figure 1(b)—with an uptick in permeability at 50 bar. These results suggest that a significantly higher pressure was necessary to drive molecule permeability upward most likely due to the presence of strong interactions between SO$_2$ and MIL-160. Such observations suggest that potential inhibition of permeation could occur due to clogging of the pore structure as well as departure from ideal gas behaviour respectively, ultimately hindering the feasibility of implementing a MIL-160 membrane for gas separations involving relatively high concentrations of SO$_2$.64

Predicted permeabilities of the simulated gas species were found to vary independently of the kinetic diameter of the simulated specie. This finding was expected as the aperture sizes of MIL-160 are approximately 5.2 Å and 2.4 Å, both falling outside of the range of critical diameters of the sampled gas molecules known to be ranging from 3.17 Å to 3.80 Å, respectively.65

Diffusivity values were also calculated at both high- and low-pressure regimes and are shown in Figure 1(d). Each gas molecule displayed a rise in diffusivity as simulation pressure increased thus concurring with increases in permeability and decreases in gravimetric solubility respectively, i.e., higher simulation pressures eventuated higher throughputs of gas molecules diffusing through the membrane. Moreover, we found that the classically described, i.e., non-reactive potential of each gas molecule impacted trends in diffusivity that dictated individual gas separation capabilities of MIL-160. Specifically, oxygenated gas species showed lower diffusivities at both high- and low-pressure regimes further highlighting the inhibitory role of energetically favourable interactions between MIL-160 and more electronegative gas species such as CO$_2$ and SO$_2$, CH$_4$, NO$_2$, and NO all known to have diffusivities nearly twice those of the other gas molecules at 50 bar. CH$_4$ showed substantially higher diffusivity—over five times higher than values calculated for CO$_2$, NO$_2$, and NO and three orders of magnitude higher than that calculated for SO$_2$—even in vacuum conditions, all relative to the oxygen-containing gas molecules. This result indicates that a MIL-160 membrane has the potential to be operable across a wide range of pressures without significant degradation of its performance; stable operability in varied pressure regimes of materials implemented in selective uptake of target greenhouse gases is regarded as a critical feature in many gas separations processes in which the separation capability of adsorbent materials relies heavily on dynamic variations in operating pressure, i.e., PSA processes.24,67

Density of the tested gas molecules in the lateral direction of the simulation box as well as visualization of gas permeation processes provided further insights into the effect of individual gas molecule chemistry on permeability and sorption characteristics (Figure 2). Analysis showed that gas molecule densities within the MIL-160 membrane varied significantly across pressure regimes for less electronegative gas species like CH$_4$, NO$_2$, and NO. This is contrary to the finding of the gas molecule density which remained relatively high at all pressures and for more electronegative gas species such as SO$_2$ and CO$_2$ to a lesser extent, respectively. The higher molecular packings of more electronegative gas species SO$_2$ and CO$_2$ are likely the result of relatively strong electrostatic interactions between gas molecules within the MOF membrane cage structures that provide energetically favorable configurations in which nearby molecules can interact.68

We also found that the high binding affinities of electronegative gas molecules to the MIL-160 membrane caused high densities of SO$_2$ within the membrane itself that are inhibitory to gas permeation even at vacuum conditions. Further, an excessively high density of gas molecules that hindered MIL-160 performance was recorded at 50 bar for CO$_2$. The characteristic spikes in gas molecule density—i.e., a sharp increase in gas molecule density and subsequent sharp decrease indicating a locally high molecule concentration—at 6 nm, the MIL-160 membrane entrance, were observed only for both CO$_2$ and SO$_2$ at 50 bar corresponding to severe concentration polarization effects. This indicates significant clogging that could occur upon such gas interactions with the constructed membrane presumably to occur due to highly favorable electrostatic interactions undergone locally at pressures where the diffusivity is not sufficient to overcome such interactions.64 This finding emphasizes that MIL-160 is not only suited for gas separations processes but further, that critical separation criteria herein defined as fundamental differences in properties of the gases simulated could be to reflect differences in gas molecule binding affinities, all in varied operating pressures. Thus, it is envisioned that a MIL-160 membrane could serve a wide range of gas separation purposes by balancing the operating pressure of the membrane system with tradeoffs in target gas molecule sorption selectivity and based on differences in gas molecule binding affinities respectively. The tradeoffs in operating pressure and gas molecule binding affinity have been exploited in commercially viable gas separations processes such as the ones employing PSA methods.

Membrane permeation and sorption of CO$_2$-containing gas mixtures.
We further tested the extended feasibility of a MIL-160 membrane in selectively removing dilute CO$_2$ from other industrially relevant gases. Although many definitions have previously been ascribed, we define dilute CO$_2$ as 5 mol% of each binary gas mixture, thus comprising a concentration that is within range of typical compositions studied in dilute gas separations$^6$. The concentrations studied herein, i.e., conditions in which CO$_2$ is dilute compared to either NO$_2$ or NO, lend our results applicability in the potential employment of MIL-160 in the treatment and containment of off-gas produced from the dissolution of nuclear spent fuel$^7$. For instance, nuclear fuel is often dissolved in nitric acid, the process leading to a significant amount of NO$_x$ contaminants as well as CO$_2$$^7$. The mitigation of such contaminants reaching the atmosphere is necessary to aid alternative energy industries in attaining higher degrees of sustainability$^7$. The extended analyses are meant to support emerging CCS technologies targeting uptake of CO$_2$ at dilute concentrations and to further extend the application profiles at large point sources of greenhouse gas emissions like power plants$^5$-7 and chemical refineries$^6$, $47$, $72$-$74$. For the analyses, the MD simulations included permeation and sorption processes of gas mixtures comprised of 5 mol% CO$_2$ with balances comprised of 95 mol% CH$_4$, 95 mol% SO$_2$, 95 mol% NO$_2$, and 95 mol% NO respectively with the simulations carried

![Fig 2. (i) Initial configuration at 1 bar, (ii) steady-state configuration at 1 bar, and (iii) number density of gas species at steady state relative to lateral direction of the simulation box at varied simulation pressures for (a) CO$_2$, (b) CH$_4$, (c) SO$_2$, (d) NO$_2$, and (e) NO.](image-url)
out at 0.2, 0.5, 1, 5, and 50 bar to corroborate single-component gas permeation results. The above gas mixtures were chosen to mimic conditions in which the target molecule i.e., CO$_2$ corresponds to physical scenarios that are representative of current challenges in gas separation technologies$^{6,73}$.

The sorption selectivity, permeselectivity, and diffusivity selectivity of each gas species relative to CO$_2$ are shown in Figure 3. Analysis of selectivity at steady-state sorption and permeation regimes and varied pressures including vacuum conditions and high-pressure conditions confirmed that the varied chemistries of the simulated gas molecules endowed the MOF membrane with different and very specific separation criteria. Specifically, results showed that adsorption processes were related to the thermodynamic preferably of gas molecule binding capabilities, i.e., essential differences in MIL-160 binding affinity. This finding further supported and emphasized the selective adsorptive gas separations processes made possible through the MOF defined membranes, which is consistent with work previously reported on MIL-160 membranes detailing differences in strength of MOF-gas molecule interactions as the most suitable basis for gas separations performed via MIL-160 membranes$^{40,42,75}$.

Figure 3(a) showed that the selectivity of gas molecule gravimetric solubility varied significantly across gas species and pressure regimes, respectively. The membrane exhibited high solubility selectivity for SO$_2$ over CO$_2$ at all pressures simulated, congruent with our own analysis that MIL-160 possesses a higher binding affinity for SO$_2$ than it did for CO$_2$. The selectivity of the gravimetric solubility of SO$_3$ remained an order of magnitude greater than the selectivities of all other gases sampled throughout high-and-low-pressure regimes, consistent with previous findings that MIL-160 is potentially applicable in the selective uptake of SO$_2$$^{75}$. Meanwhile, the selectivity of the solubility of CH$_4$ relative to CO$_2$ was relatively low at all pressures being evaluated, thus suggesting that differences in binding affinity for MIL-160 between CH$_4$ and CO$_2$ could potentially allow for the selective removal of CO$_2$ from CH$_4$. This finding is especially important considering that the separation of CO$_2$ from CH$_4$ has been identified as a particularly crucial step in the upgrade of biogas—organic material often derived from agricultural waste, municipal waste, and plant material—to value-added chemicals$^{76}$ and hit at the potential of MIL-160 as a promising candidate in large-scale separations for biogas upgradation technologies.

The solubility selectivity values of NO$_2$ and NO compared to CO$_2$ were calculated to vary across the pressure regimes being studied. At vacuum and atmospheric conditions for instance, MIL-160 exhibited a slightly higher solubility for NO$_2$ and NO than it did for CO$_2$. However, selectivities of NO$_2$ and NO were found to decrease sharply at 50 bar presumably due to the increased simulation pressure overcoming thermodynamic barriers to desorption of NO$_2$ and NO to a greater extent than those of CO$_2$, thus resulting in CO$_2$ binding to MIL-160 more stably. These findings are supported by our single-component gas simulations (Fig 1(b)) in which the solubilities of NO$_2$ and NO were found to be less than that of CO$_2$ at high pressures. The decrease in solubility of both NO$_2$ and NO likely coincides with the increase in permeability at pressures that are high enough to overcome the respective thermodynamic barriers associated with the desorption of NO$_2$ and NO from the MIL-160 membrane.

Figure 3(b) shows the calculated permselectivity values of each gas species at varied pressures relative to CO$_2$, with analysis supporting the strong pressure and gas composition dependence on the gas separation characteristics of MIL-160. Our analysis also indicated that the permselectivity of respective gas molecules varied across orders of magnitude as the tradeoff between high MOF-gas molecule affinity and low permeability proved paramount in extended membrane’s gas separation applicability. Less electronegative gas species like CH$_4$, NO$_2$, and NO all demonstrated complex pressure-dependent relationships with respect to calculated permselectivity values. In particular, the permselectivity
profiles of each gas were found to correlate with the respective solubility selectivity profile. Significant changes in permselectivity occurred when pressures were sufficient in overcoming barriers associated to the desorption processes. For example, a notable change in permselectivity was calculated at a lower pressure for CH\textsubscript{4} presumably due to the low affinity of MIL-160 for CH\textsubscript{4} and higher pressures required to initiate desorption of the slightly more electronegative gas species. SO\textsubscript{2} showed the lowest degree of permeability relative to less electronegative gas species in mixtures. Additionally, the permselectivity of SO\textsubscript{2} relative to CO\textsubscript{2} was found to be undefined at pressures 0.5 bar and 50 bar, i.e., no CO\textsubscript{2} permeated through the MIL-160 membrane. Zerapproaching permeability of dilute CO\textsubscript{2} provided further evidence that pore clogging caused by SO\textsubscript{2} leads to logistical problems in the separability of CO\textsubscript{2} from a highly electronegative gas when using a hydrophilic MOF support.

The kinetic diameters of the simulated gases were again predicted to have no measurable effect on the separation capabilities at the membrane interface itself. Moreover, neither the sorption selectivity nor the permselectivity of each gas species was correlated to the kinetic diameters of the greenhouse gases molecules; this was presumably due to pore geometry of MIL-160, i.e., the aperture sizes of MIL-160 are known to be outside the range of kinetic diameters of the gas molecules sampled in our study. MIL-160 aperture sizes are approximately 5.2 Å and 2.4 Å, while the kinetic diameter of each gas simulated is well within that range\textsuperscript{42}; thus, our analysis demonstrated that the aperture sizes of MIL-160 plays a less significant role in separations processes of CO\textsubscript{2} from other greenhouse gases than do the varying strengths of MOF-gas molecule electrostatic interactions.

Our analysis of the diffusivity selectivity of each gas species relative to CO\textsubscript{2} are shown in Figure 3(c); it was found that the selectivity trended upward as simulation pressure increased, with the exception of SO\textsubscript{2} that had a prohibitively high gravimetric solubility in MIL-160. On the other hand, the MIL-160 membrane showed high selectivity of CH\textsubscript{4} relative to CO\textsubscript{2} at all pressures tested, owing to the pronounced difference in respective gas molecule binding affinity to MIL-160. The pressure dependence of the diffusivity selectivity values of NO\textsubscript{2} and NO was found to lie in a critical range that ultimately could determine the applicability of MIL-160 in particular gas separations applications. Specifically, the diffusivity selectivity of NO\textsubscript{2} was found to be less than 1, i.e., favor CO\textsubscript{2}, at low pressures but was calculated to approach 10 at 50 bar; therefore, the operating pressure of the membrane system can potentially be altered to manipulate desired gas separation selectivities of a MIL-160 membrane. Such pressure-based functionality forms the basis of PSA processes in which MIL-160 could be implemented where the separation of CO\textsubscript{2} from NO\textsubscript{x} is of critical importance, like flue gas separations and treatment of off-gas produced from used nuclear fuel dissolution\textsuperscript{70, 71, 77}.

Competitive adsorption processes within the MIL-160 membrane.
The dynamic sorption and permeation profiles of the simulated gas mixtures at pressure 50 bar are shown in Figure 4, while the similar profiles at pressures 0.2, 0.5, 1, and 5 bar are shown in Figures S.6-S.9 in Supporting Information. Analysis indicated that the separability of dilute CO\textsubscript{2} from other greenhouse gases at the molar compositions sampled in our study hinges on the...
ability of CO$_2$ to displace already adsorbed gas species. The higher concentrations of CH$_4$, SO$_2$, NO$_2$, and NO molecules in respective simulations eventuated the rapid flooding of the MIL-160 membrane with such molecules within approximately 0.5 ns of simulation followed by a slower dynamic response—about 5 ns—in which the number of CO$_2$ molecules within the membrane increased until steady-state concentrations within the membrane were attained.

At steady-state concentrations within the MIL-160 membranes, the local composition of each binary mixture was determined to reflect the affinity with which MIL-160 was able to bind respective gas molecules. While CO$_2$ comprised only 5 mol% of the gas baths of each composition, we found that at steady-state at 50 bar CO$_2$ accounted for approximately 20 mol% of the molar com-position of gas within the MIL-160 membrane in CH$_4$/CO$_2$ and NO/CO$_2$ gas mixture simulations and about 16 mol% of the molar composition of gas within the MIL-160 membrane in the NO$_2$/CO$_2$ gas mixture simulation. At the same conditions, CO$_2$ accounted for only about 0.5 mol% of the molar composition of gas within the MIL-160 membrane in SO$_2$/CO$_2$ gas mixture simulation, thus pointing to the clear thermodynamic preferability of MIL-160 for SO$_2$ over CO$_2$.

Our results are in good agreement with values calculated from both gas simulation and experimental gas sorption studies previously reported in literature (Table 1), with the specific analysis reproducing adsorption capacities for CH$_4$ and SO$_2$ at similar temperature and pressure conditions when compared to those published in recent gas separations papers$^{40, 75}$. The adsorption capacity of CO$_2$ within the MIL-160 membrane at specified temperatures and pressures, however, was found to deviate from previously reported values; our analysis showed that MIL-160 possesses a lower adsorption capacity for CO$_2$ than did other gas simulation studies$^{40, 75}$. This discrepancy could be due to differences between physical scenarios defined in this work. Specifically, in our analysis, gas baths were maintained at a constant pressure without regard for controlling pressure within the MIL-160 membrane, while other authors have employed grand canonical Monte Carlo (GCMC) methods with simulation pressure controlled within the membrane$^{40}$. To our knowledge, no data exist with which to compare our adsorption capacity values of NO$_2$ and NO, but comparison to similar analyses for different MOF materials confirms that MIL-160 has potential to perform at least as well as such MOFs$^{79, 81}$.

| Gas species | Calculated gas uptake (kg gas kg$^{-1}$ MIL-160) @ temperature, pressure | Previously reported gas uptake (kg gas kg$^{-1}$ MOF) @ temperature, pressure | MOF | References |
|-------------|-------------------------------------------------|-------------------------------------------------|-----|------------|
| CO$_2$      | 7.09 x 10$^{-2}$ @ 300 K, 1 bar                | 1.85 x 10$^{-1}$ @ 298 K, 1 bar                | MIL-160 | 75 |
|             | 3.76 x 10$^{-2}$ @ 300 K, 0.5 bar              | 1.41 x 10$^{-1}$ @ 293 K, 0.5 bar *            | MIL-160 | 78 |
|             | 1.31 x 10$^{-1}$ @ 300 K, 0.2 bar              | 7.70 x 10$^{-2}$ @ 293 K, 0.2 bar *            | MIL-160 | 78 |
| CH$_4$      | 1.26 x 10$^{-2}$ @ 300 K, 1 bar                | 1.28 x 10$^{-2}$ @ 303 K, 1 bar                | MIL-160 | 40 |
|             | 3.58 x 10$^{-1}$ @ 300 K, 1 bar                | 4.03 x 10$^{-1}$ @ 298 K, 1 bar                | MIL-160 | 75 |
| SO$_2$      | 3.35 x 10$^{-1}$ @ 300 K, 0.5 bar              | 4.03 x 10$^{-1}$ @ 293 K, 0.5 bar *            | MIL-160 | 41 |
|             | 3.12 x 10$^{-1}$ @ 300 K, 0.2 bar              | 3.78 x 10$^{-1}$ @ 293 K, 0.2 bar *            | MIL-160 | 41 |
| NO$_2$      | 7.75 x 10$^{-2}$ @ 300 K, 1 bar                | 6.49 x 10$^{-1}$ @ 298 K, 1 bar                | MFM-300(Al) | 79 |
| NO          | 7.67 x 10$^{-2}$ @ 300 K, 1 bar                | 9.30 x 10$^{-1}$ @ 298 K                       | Rh/MOF-177 | 81 |

Previously reported gas uptake (kg gas kg$^{-1}$ MOF) @ temperature, pressure. * indicates values derived from empirical data.
Moreover, our unique approach has the advantage of allowing for complex analysis of multi-component gases which are not easily attainable through studies involving potential of mean force (PMF) analysis. Specifically, when comparing our membrane system to the membrane systems studied by Khakpay et al., we make two important distinctions between a MIL-160 membrane and nanoporous graphene (NPG) and nanoporous graphene oxide (NPGO) sheets that ultimately confound the simplicity with which a PMF analysis could be implemented for the MIL-160 membrane. First, the inherent cage-like geometry of the MIL-160 membrane poses geometrical limitations on the umbrella sampling routine that would be invoked to determine the binding affinity of a particular gas molecule to MIL-160. It is likely that the interior cage structure of this MOF is not sufficiently large to allow for proper sampling of PMF as a gas molecule is moved away from a particular binding sight. Secondly, the complexity of the chemical structure of MIL-160 compared to those of NPG and NPGO sheets inundates the number of potential binding sites that could be considered of interest when undertaking a PMF analysis, with the subsequent computational load being multiplied when extended to five gas species.

Our study complements current work focusing on gas separation performance of emerging MOF materials, while being insightful with respect to the expanding range of gas separations in which MIL-160 could be advantageously implemented. The identification of atomic-level phenomena that are determinant in the efficiency of a MIL-160-based membranes are further adding to the body of work previously published and highlighting hybrid supports such as polydopamine-modified aluminum oxide discs to achieve efficient separations of xylene isomers for instance. We envision that MIL-160-based membranes prepared on a wide range of polymeric or ceramic supports can be produced to meet a number of industrially relevant gas separations. Additionally, we contend that MIL-160 materials have the potential to be particularly beneficial in separation of target gases based on reversible, pressure- and temperature-dependent differences in gases molecule binding affinities. Similar strategies have already been employed for the efficient, low-energy uptake and full regeneration of water vapor and relatively at mild temperatures.

Conclusions

Our results showed that MIL-160 has extended potential for processes designed to separate gas species with strongly differing electronegativities and thus different binding affinities of such gases to MIL-160 membrane itself. Specifically, we found that MIL-160 is capable of selectively binding dilute CO\textsubscript{2} in gas mixtures comprised of less electronegative gas species—CH\textsubscript{4}, NO\textsubscript{2}, and NO, respectively—at varied pressures which strongly alter the separation capabilities of the membrane itself as well as influence membrane applicability for specific uses in industrial settings like biogas upgradation and treatment of off-gas from used nuclear fuel dissolution. Further, our strategy was instrumental in exemplifying the competitive adsorption processes between greenhouse molecules within the MIL-160 membrane that were principal to the gas separation capability of the membrane itself. Our work herein demonstrates the significance of MD simulations in the identification of critical separation criteria, i.e., selective adsorption via MOF-gas molecule interactions that lay the foundation for scalable, sustainable gas separations processes that will meet a growing global energy demand while reducing the unwanted societal effects of anthropogenic greenhouse gas emission.

Author Contributions

All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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