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Research Article

Application of MD Simulations to Predict Membrane Properties of MOFs

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Metal organic frameworks (MOFs) are a new group of nanomaterials that have been widely examined for various chemical applications. Gas separation using MOF membranes has become an increasingly important research field in the last years. Several experimental studies have shown that thin-film MOF membranes can outperform well known polymer and zeolite membranes due to their higher gas permeances and selectivities. Given the very large number of available MOF materials, it is impractical to fabricate and test the performance of every single MOF membrane using purely experimental techniques. In this study, we used molecular simulations, Monte Carlo and Molecular Dynamics, to estimate both single-gas and mixture permeances of MOF membranes. Predictions of molecular simulations were compared with the experimental gas permeance data of MOF membranes in order to validate the accuracy of our computational approach. Results show that computational methodology that we described in this work can be used to accurately estimate membrane properties of MOFs prior to extensive experimental efforts.

1. Introduction

Membrane-based gas separation has several advantages over traditional separation techniques such as energy efficiency, smaller carbon footprint, and environment friendly nature of operation. Due to these advantages, membrane-based gas separation has received significant interest from academy and industry. Membrane-based gas separations include several industrially and economically important processes such as air purification, flue gas treatment, natural gas purification, hydrogen recovery from plant, and refineries. Design and development of new membrane materials that can achieve these gas separations with high performance are crucial. Although thousands of new materials have been synthesized to date, it has been recently reported that more than 90% of current commercial membranes are still made from fewer than ten materials, most of which are being in use for decades [1]. These membranes are generally made of polymers. Polymer membranes have the advantages of easy fabrication and scalability. However, they have a fundamental trade-off between gas selectivity and permeability. Robeson [2] used a large collection of experimental data and showed that there is an inverse relationship between selectivity and gas permeability of polymer membranes. Nanoporous materials such as zeolites are good alternatives to polymers. Zeolites are known to have high thermal and mechanical stability. They can be used under a wide range of pH and temperature conditions. Although many zeolite membranes have been tried in various gas separation applications, their complicated fabrication processes, high manufacturing costs, and challenges in scale-up prevented the wide usage of zeolite membranes in this area [3].

In the last decade, a new group of nanoporous materials named as metal organic frameworks (MOFs) has emerged as a strong alternative to more traditional nanoporous materials such as zeolites. MOFs are composed of metal complexes that are linked by organic ligands to create highly porous frameworks [4]. Combination of various metals and organic linkers leads to a large diversity of materials with different geometry, size, and functionality [5]. Therefore, thousands of MOF materials have been reported in the literature. MOFs have permanent pores, large varieties in pore sizes ranging from micro- to mesoscale, low densities, very large surface areas, and reasonable thermal and mechanical stabilities [6–8].

These properties make MOFs attractive materials in several chemical applications such as gas storage [9], gas separation [10], catalysis [11], and drug delivery [12]. Among these areas, gas separation can be considered as the most mature one since a large number of experimental studies have been carried out for adsorption and membrane-based gas separations by MOFs [13–15]. If the appropriate metal complexes and organic ligands are chosen, MOFs with predefined pore sizes and shapes can be created for specific gas separations. The ability to fine tune structural properties of MOFs such as pore sizes and shapes offers a great advantage to use these materials as membranes because pore characteristics play an important role in determining separation performance of materials.

Although thousands of MOF materials exist in the literature, only a few different types of MOFs were used to make membranes. IRMOF-1, ZIF-8, and ZIF-90 can be listed as the most widely studied MOF membranes. IRMOF-1 (isoreticular metal organic framework), also known as MOF-5, is the first continuous and well-intergrown MOF membrane reported in the literature [16]. Zeolite imidazolate frameworks (ZIFs) are a subclass of MOFs which are tetrahedral networks constructed by linkage of transition metals (Zn, Co, Fe, and Cu) and imidazolate (Im) type linkers [17]. Combinations of transition metals with various imidazolate linkers lead to synthesis of a large diversity of ZIFs. ZIFs are well known with their good chemical stability and permanent porosity which make them strong candidates for membrane applications [18, 19]. ZIF-8 [20–23], ZIF-69 [24, 25], ZIF-78 [26], ZIF-90 [27], and ZIF-95 [28] membranes were fabricated and their gas permeances were experimentally measured by different research groups. Among these membranes, ZIF-90 molecular sieve membrane displayed high thermal and hydrothermal stability in addition to high H_2 selectivity [27]. ZIF-95 membrane was reported to be highly permeable and it showed by far the highest H_2/CO_2 selectivity compared to other fabricated MOF membranes [28].

The very large number of distinct MOFs that are available in the literature presents both a challenge and an opportunity for the development of MOF membranes. The wide range of available pore sizes, topologies, and chemical functionalities strongly suggests that many MOFs would have useful properties as gas separating membranes. However, experimental fabrication of thin-film membranes from thousands of new materials is challenging. It is impractical to fabricate and test the performance of every single MOF membrane in laboratories. Computational approaches that can predict gas separation performance of MOF membranes prior to experiments would be highly useful. In this study, we described a computational approach that combines Monte Carlo and Molecular Dynamics simulations to predict gas permeance data of fabricated MOF membranes. We then compared gas permeance data obtained from molecular simulations with the experimentally measured one to validate the accuracy of our computational method. This approach will be highly useful for quick screening of MOFs to identify the most promising membrane candidates for further experimental studies.

Table 1: Potential parameters used in molecular simulations.

Gas	ε/k_B (K)	σ (Å)	q (e)
CH_4	148.0	3.73	—
C (in CO_2)	27.00	2.80	+0.70
O (in CO_2)	79.00	3.05	−0.35
H_2	34.2	2.96	—
He	10.90	2.64	—
N (in N_2)	36.4	3.318	−0.40
COM (in N_2)	0.0	0.0	+0.80

2. Computational Details

2.1. Atomic Models for MOFs and Gases. Eight MOFs were examined in this work as membranes. These were IRMOF-1, ZIF-8, ZIF-69, ZIF-78, ZIF-90, ZIF-95, Ni-MOF-74, and MIL-53(Al). Atomic positions of MOFs were taken from the X-ray diffraction data of experiments deposited to Cambridge Crystallographic Data Center (CCDC) [29]. All structures were assumed to be rigid in molecular simulations. Universal Force Field (UFF) [30] was used for the potential parameters of all MOFs except IRMOF-1 for which Dreiding [31] force field was used. Molecular simulations carried out using these force fields were shown to give good agreement with experimental gas uptake data of several MOFs [32]. Spherical Lennard-Jones (LJ) 12-6 potential was used to model H_2 [33], CH_4 [34], and He [35] gases. CO_2 was represented as a rigid three-site molecule with partial point charges located at the center of each site [36]. N_2 molecule was modeled as a three-site model with two sites located at two N atoms and the third one located at its center of mass (COM) with partial point charges [37]. Table 1 summarizes the potential parameters used for gas molecules in our molecular simulations. The Lorentz-Berthelot mixing rules were employed in all molecular simulations.

In order to compute the electrostatic interactions between gas molecules having quadrupole moment (CO_2 and N_2) and MOF atoms, partial point charges were assigned to MOFs. The partial charges of ZIF-8, ZIF-69, and ZIF-78 were assigned using CBAC (Connectivity Based Atomic Charge) method [38] with slight variation to make the total charge zero whereas atomic partial charges for IRMOF-1, Ni-MOF-74, MIL-53(Al), and ZIF-95 were calculated using EQeq (Extended Charge Equilibration) method [39]. Both charge assignment methods were previously tested in the literature for MOFs and found to give good agreement with the quantum mechanical (QM) charge calculation methods. Atomic partial charges for ZIF-90 were taken from a recent work of Watanabe et al. [40], who showed that REPEAT charges gave the best results for producing the CO_2 adsorption isotherm in ZIF-90 among the several quantum mechanical calculation-based point charges that they had tested.

2.2. Details of Molecular Simulations. Single-component adsorption of gases was computed using Grand Canonical Monte Carlo (GCMC) simulations. Simulations based on GCMC have been compared rather successfully with

the adsorption experiments for several nanoporous materials including MOFs [43, 44]. In the grand canonical ensemble, the temperature, volume, and chemical potential are fixed and the number of particles is allowed to fluctuate during the simulation at an imposed temperature and chemical potential. In our GCMC simulations, we calculated the number of adsorbed gas molecules per unit cell of the MOF structure at fixed temperature and pressure. The statistical mechanical basis of GCMC simulations and more details can be found elsewhere [45]. Simulation box was consisted of $2 \times 2 \times 2$ unit cells and periodic boundary conditions were applied to simulate the bulk phase. 1.5×10^7 equilibration and 1.5×10^7 production steps were used. Four types of different moves which are insertion, deletion, rotation, and translation were employed during the simulations. The cut-off distance for truncation of the intermolecular interactions was set to 13 Å.

GCMC simulations were performed at the feed and permeate pressures of the membrane. After feed and permeate site concentrations (c_i^{feed} and c_i^{perm}, resp.) of gases were calculated, we used shell model [46] which approximates the concentration gradient, ∇c, using the boundary loadings (where L represents the thickness of the membrane), and evaluates the diffusivity at the mean adsorbate loading:

$$\nabla c \cong \frac{c_i^{\text{perm}} - c_i^{\text{feed}}}{L}. \quad (1)$$

The shell model has been tested in a previous study [47] and gave very similar results to direct integration technique when the net concentration gradient across the membrane is mild and the diffusion coefficients are only weakly dependent on the adsorbate concentration. Since using a shell model is far more convenient than performing larger numbers of calculations, all permeation data were computed based on the shell model.

Equilibrium Molecular Dynamics (EMD) simulations in NVT ensemble (NVT = constant number of molecules, constant volume and temperature) were performed to calculate the corrected diffusivity ($D_{0,i}$) of gases at average loadings calculated from GCMC simulations performed at feed and permeate site pressures. The corrected diffusivity describes the collective motion of the adsorbed molecules. It is calculated based on the number of molecules (N), time (t), and three-dimensional position vector of molecule l of species i at time t, $r_{il}(t)$ [45]:

$$D_{0,i} = \lim_{t \to \infty} \frac{1}{6Nt} \left\langle \left(\sum_{l=1}^{N_i} \left[r_{il}(t) - r_{il}(0) \right] \right)^2 \right\rangle. \quad (2)$$

During EMD simulations, temperature was kept constant by applying Nosé-Hoover thermostat algorithm. At least 20 trajectories were collected from EMD simulations and average corrected diffusivity was reported. The transport diffusivity (D_t) was obtained by multiplying the corrected diffusivity (D_0) with thermodynamic correction factor ($\partial \ln f / \partial \ln c$) [48], the partial derivative relating the adsorbed gas amount, c, and bulk phase fugacity, f:

$$D_t(c) = D_0(c) \cdot \frac{\partial \ln f}{\partial \ln c}. \quad (3)$$

The thermodynamic correction factor is fully defined once the single-component adsorption isotherm is known. Steady state fluxes of each gas molecule through a MOF material were calculated based on Fick's Law [48]:

$$J = -D_t(c) \cdot \nabla c. \quad (4)$$

Gas flux (J) in MOFs was then converted to gas permeance (P) by dividing with the pressure drop (ΔP) and reported in mol/m^2/s/Pa:

$$P = \frac{J}{\Delta P}. \quad (5)$$

In some experimental studies, gas permeability (mol/m/s/Pa) is reported rather than gas permeance. Gas permeability can be simply calculated by normalizing the permeance with the thickness of the membrane as follows:

$$\text{Permeability} = \frac{J}{\Delta P / L}. \quad (6)$$

In the case of gas mixtures, permeances of each gas species were computed using mixture GCMC and EMD simulations. In mixture GCMC simulations, composition of the feed gas was specified as an input and another trial move, exchange of molecules, was also performed. The adsorbed loadings of the gas components (c_i, c_j) computed from GCMC simulations were used as an input in EMD simulations and self-diffusivities ($D_{i,\text{self}}$) of species were computed directly at these adsorbed loadings. Gas permeabilities of mixture were calculated as follows and converted to permeances as shown above [49, 50]:

$$\text{Permeability}_i = \frac{\phi \cdot D_{i,\text{self}} \cdot c_i}{f_i}. \quad (7)$$

In this equation, ϕ is the fractional pore volume of the MOF material taken from experimental studies, $D_{i,\text{self}}$ is the self-diffusivity of species i in the mixture (m^2/s), c_i is the concentration of species i at the feed side of the membrane (mol/m^3), and f_i is the bulk phase fugacity of the species i (Pa) [50]. All molecular simulations were carried out at the same membrane operating conditions (feed pressure, permeate pressure, and temperature) with the experiments to make an accurate comparison between simulations and experiments. These operating conditions are shown in Table 2.

3. Results and Discussions

We calculated both single-gas and mixture permeances of MOF membranes and compared our results with the available experimental data. Figure 1 shows single-component gas permeances of CH_4, H_2, CO_2, N_2, and He through three different MOF membranes, IRMOF-1, Ni-MOF-74, and MIL-53(Al). Considering the fact that the only experimental

Table 2: Properties and permeance measurement conditions of MOF membranes.

MOF membrane	Measured gas permeances	P_{feed} (bar)	$P_{permeate}$ (bar)	T (°C)	Membrane thickness (μm)	Reference
IRMOF-1	CH_4, H_2, CO_2, N_2	1.06	Vacuum	25	25	[16]
Ni-MOF-74	CH_4, H_2, CO_2, N_2	1.8	1	25	25	[41]
MIL-53(Al)	He, N_2, CO_2	0.7	Vacuum	25	60	[42]
ZIF-69	CH_4, H_2, CO_2	1	Vacuum	25	50	[24]
	N_2				40	[25]
	CH_4/CO_2: 50/50				40	
	CO_2/N_2: 50/50				40	
ZIF-78	CH_4, H_2, CO_2, N_2	2.5	1	25	25	[26]
	H_2/CH_4: 50/50	2				
	H_2/CO_2: 50/50	2				
	H_2/N_2: 50/50	2				
ZIF-90	CH_4, H_2, CO_2, N_2	1	Vacuum	200	20	[27]
	H_2/CH_4: 50/50					
	H_2/CO_2: 50/50					
	H_2/N_2: 50/50					
ZIF-95	CH_4, H_2, CO_2, N_2	1	Vacuum	325	30	[28]
	H_2/CH_4: 50/50					
	H_2/CO_2: 50/50					
	H_2/N_2: 50/50					
ZIF-8	H_2	1	Vacuum	25	12	[20]
	H_2/N_2: 50/50					
	H_2/CO_2: 50/50					
	H_2/CH_4: 50/50					
	H_2	1	Vacuum	25	15	[21]
	H_2	1	Vacuum	25	11	[22]
	H_2	2.76	1.76	25	10	[23]

input of our molecular simulations is the XRD structures of MOF materials, there is a very good agreement between experimental measurements and predictions of our molecular simulations. The agreement is remarkably good for permeances of N_2 and H_2 in IRMOF-1, CH_4, H_2, CO_2, and N_2 in Ni-MOF-74, and He in MIL-53(Al). For example, Liu et al. [16] measured gas permeances of N_2 and H_2 as 1.3×10^{-6} and 2.8×10^{-6} mol/m^2/s/Pa in IRMOF-1 membrane and our molecular simulations predicted these values as 1.4×10^{-6} and 3.5×10^{-6} mol/m^2/s/Pa, respectively. Molecular simulations slightly overestimated CO_2 permeances in IRMOF-1 and MIL-53(Al) membranes. Experimentally reported gas permeances of CO_2 were 8.0×10^{-7} and 3.1×10^{-7} mol/m^2/s/Pa in IRMOF-1 and MIL-53(Al) membranes whereas simulations predicted these values as 1.9×10^{-6} and 4.0×10^{-6}, respectively.

Figure 2 compares both single-gas permeances (CH_4, H_2, CO_2, and N_2) and permeances of equimolar mixtures of CH_4/CO_2 and CO_2/N_2 through ZIF-69 membranes. There is a very good agreement between simulations and experiments for mixture permeances, especially for CO_2/CH_4. Molecular simulations generally overestimated permeances of single gases. At that point, it is important to note that single-gas permeances and mixture permeances of ZIF-69 membranes were measured in two separate experiments performed in different years as can be seen from Table 2. The difference between two sets of data can be explained by the different experimental methods used by Liu and coworkers. In their first study [24], at which single-component gas permeances were measured, *in situ* solvothermal method was used to synthesize the ZIF-69 membrane. In their second study [25], at which mixture permeances were measured, a seeded secondary growth method was used. Therefore, synthesis methods and thickness of the ZIF-69 membranes used in single-gas and mixture permeance tests were different. It was concluded that higher permeances could be obtained by the second synthesis method which was also validated by our simulation results as shown in Figure 2.

Figure 3 shows both single-gas permeances (CH_4, H_2, CO_2, and N_2) and permeances for equimolar mixtures of H_2/CH_4 and H_2/N_2 through ZIF-78 membrane. The agreement between simulations and experiments is remarkably good except one point, single-component CO_2 permeance. Simulations overestimated CO_2 permeance of ZIF-78 almost an order of magnitude, similar to the cases of IRMOF-1 and ZIF-69 as can be seen in Figures 1 and 2, respectively. Predictions of simulations for CH_4 and N_2 permeances were found to be almost the same with the experiments. For example, experimentally measured CH_4 and N_2 permeances were 1.6×10^{-8} and 1.8×10^{-8} mol/m^2/s/Pa while molecular simulations well predicted these permeances as 1.6×10^{-8}

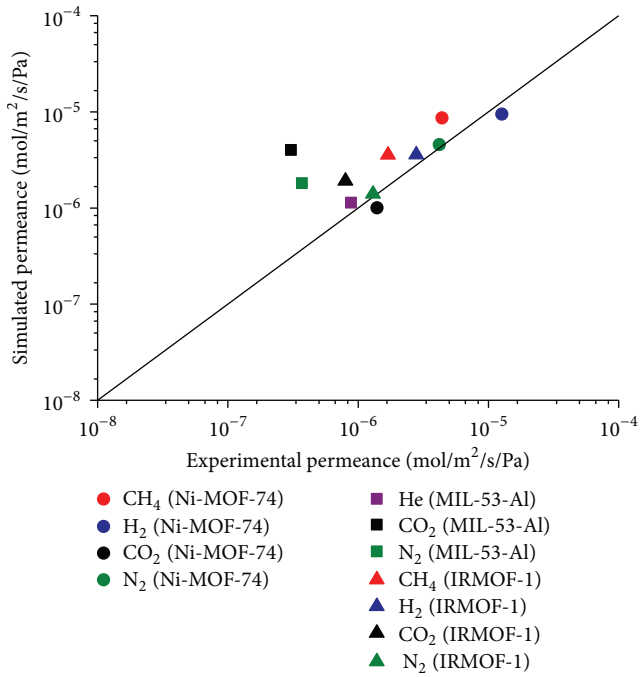

Figure 1: Comparison of our molecular simulations and experiments for single-component gas permeances through IRMOF-1, Ni-MOF-74, and MIL-53(Al) membranes.

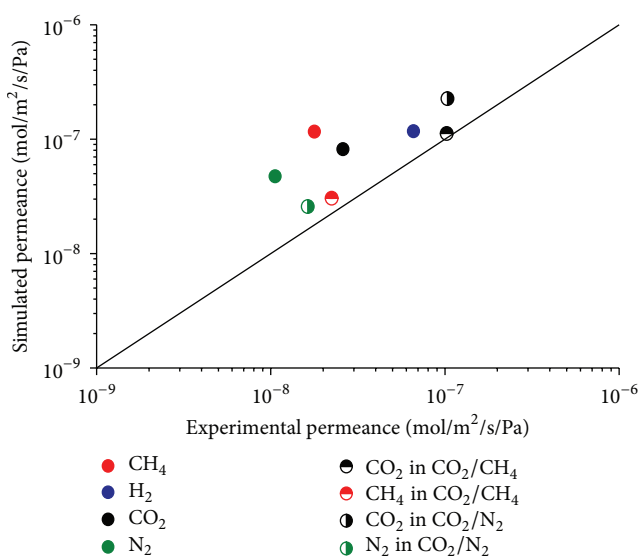

Figure 2: Comparison of our molecular simulations and experiments for single-component and mixture permeances through ZIF-69 membrane.

and 1.7×10^{-8} mol/m^2/s/Pa, respectively. Similarly, permeances of H_2/N_2 mixture were well estimated by simulations. Experimentally measured H_2 and N_2 permeances were 1.1×10^{-7} and 1.9×10^{-8} mol/m^2/s/Pa and simulations predicted these values as 1.1×10^{-7} and 1.2×10^{-8} mol/m^2/s/Pa, respectively.

ZIF-90 is one of the MOF materials that have a large amount of experimental gas permeance data. Figure 4 compares single-gas (CH_4, H_2, CO_2, and N_2) and mixture

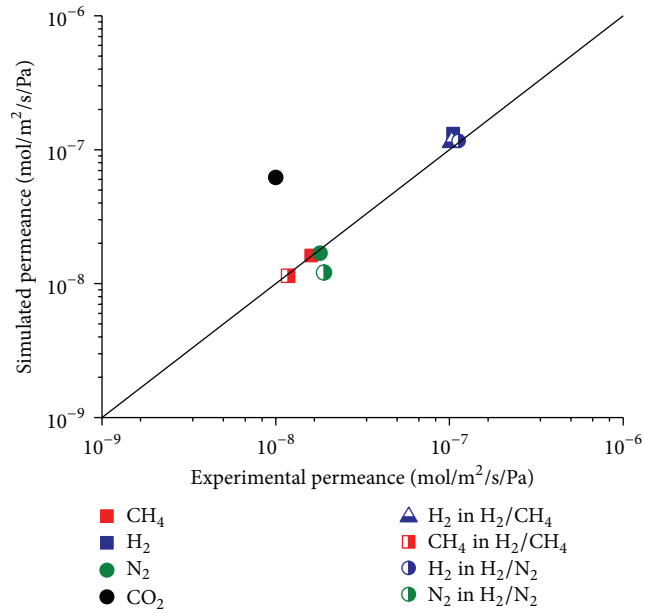

Figure 3: Comparison of our molecular simulations and experiments for single-component and mixture permeances through ZIF-78 membrane.

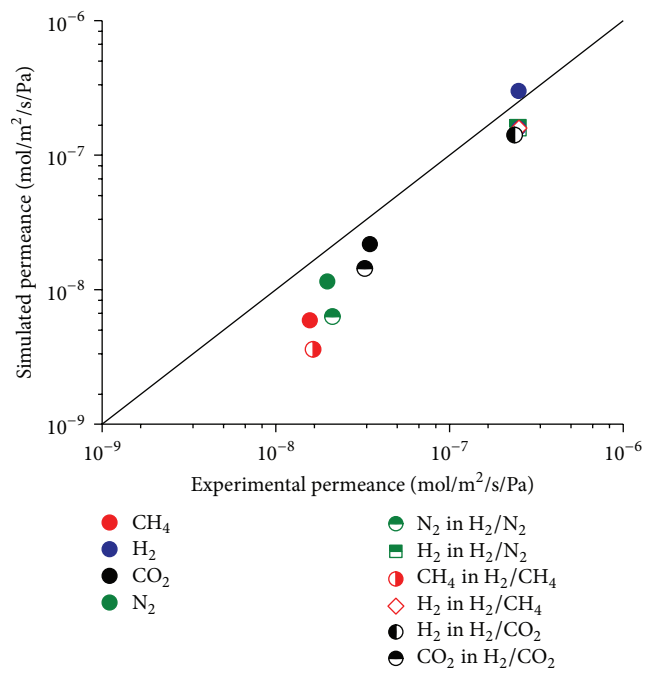

Figure 4: Comparison of our molecular simulations and experiments for single-component and mixture permeances through ZIF-90 membrane.

permeances for H_2/CH_4, H_2/CO_2, and H_2/N_2 through ZIF-90 membrane. The predictions for single-component gases, especially for CO_2 and H_2, are remarkably well. Simulations slightly underestimated single-component gas permeances of larger molecules, CH_4 and N_2. This can be explained by discussing kinetic diameters of gas molecules and pore sizes of the membrane material. The kinetic diameters of CH_4

(3.73 Å) and N_2 (3.68 Å) molecules are slightly larger than the narrow pore size of ZIF-90 membrane (3.5 Å). Our molecular simulations did not include lattice flexibility effects; therefore, permeances of gas molecules having kinetic diameters larger than the narrow pore size of ZIF-90 membrane (CH_4 and N_2) were slightly underestimated. The same discussion is valid for the mixture permeances of H_2/CH_4 and H_2/N_2. Although H_2 permeances in both mixtures were well predicted, permeances of CH_4 and N_2 were underestimated due to the same reason. The kinetic diameters of H_2 and CO_2 molecules are smaller than the narrow pore diameter of ZIF-90 membrane; therefore, both single-gas (H_2, CO_2) and mixture (H_2/CO_2) permeances of these two species were well predicted by the molecular simulations. These results suggest that molecular simulations must be used with ultimate care when estimating permeances of gas molecules that are close to or larger than the pore size of the membrane material.

We show comparison between experiments and molecular simulations for gas permeances of ZIF-95 membrane in Figure 5. Both single gas and mixtures of H_2/CO_2, H_2/N_2, and H_2/CH_4 were compared with the experimental data. Although there is a good agreement between experimental and simulated permeances of single-component CO_2 and CO_2 in H_2/CO_2 mixture, all other gas permeances were underestimated. Underestimation of single-component gas permeances of CH_4 and N_2 can be attributed to the narrow pores of ZIF-95 (3.7 Å), similar to the case of ZIF-90. Molecular simulations significantly underestimated permeances of H_2 and its mixtures. This underestimation can be explained by the competition effect between gas species in H_2-including mixtures. Molecular simulations showed that CO_2, N_2, and CH_4 gases are much more strongly adsorbed than H_2 due to the weaker interactions between H_2 and ZIF-95 framework. These strongly adsorbed gases prevent adsorption and diffusion of H_2 in the pores of the MOF and therefore molecular simulations predict very low H_2 permeances. Since our previous results showed that molecular simulations very well predict single-component H_2 permeances in IRMOF-1, Ni-MOF-74, ZIF-69, ZIF-78, and ZIF-90 membranes (as shown in Figures 1–4), it can be also argued that there may be defects in the microstructure of the fabricated ZIF-95 membrane. These defects may allow significant fluxes of small gases such as H_2 through the membrane and overestimate H_2 permeance.

It is important to discuss the assumptions associated with the computational approach that we described in this study. All molecular simulations were performed assuming rigid MOF structures, which is a widely used assumption in molecular modeling of MOFs in the literature [32]. This assumption saves tremendous computational time since MOFs are kept at their reported crystallographic structure during the simulations. The good agreement between simulated permeance data and experimentally measured one as we showed above for several MOF membranes suggests that rigid framework assumption was valid at least for the seven MOFs that were examined in this work. However, it is not possible to argue that this assumption is fully correct for all MOFs because recent studies showed that structural changes can be observed in some MOFs upon adsorption [51]. Molecular

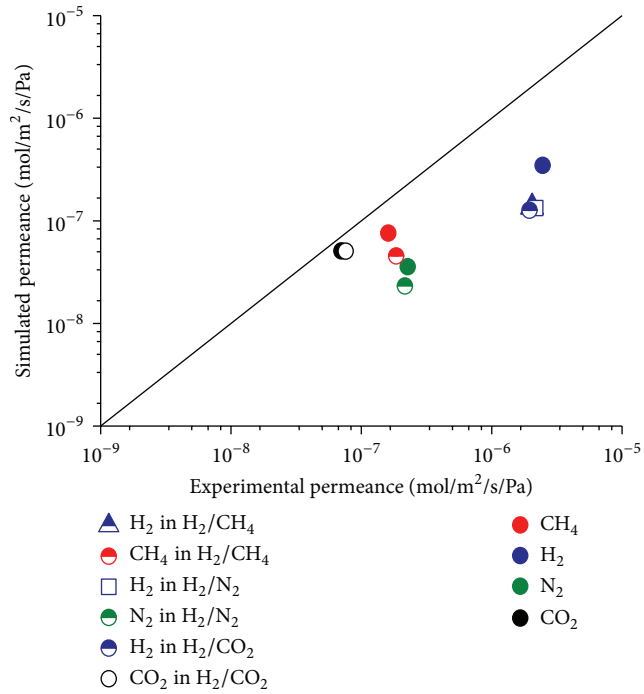

Figure 5: Comparison of our molecular simulations and experiments for single-component and mixture permeances through ZIF-95 membrane.

simulations that do not account for framework flexibility generally underestimate permeances of the gas molecules which are larger than the material's pore size. One good example is ZIF-8 membrane. Haldoupis et al. [52] predicted ideal selectivity (defined as the ratio of gas permeances) of ZIF-8 membranes for H_2/CH_4 separations using simulations and their predicted selectivities were orders of magnitude larger than the selectivities measured experimentally for ZIF-8 membranes. They attributed this discrepancy to the defects in the microstructure of the membrane since defects associated with grain boundaries can allow significant fluxes of gases through the membranes. However, their overestimated selectivities may be due to the rigid framework assumption of ZIF-8 structure. If the flexibility is not taken into account, diffusion of large gas molecules in small-pored MOFs may not be computed correctly and this can mislead to the very large membrane selectivities. For example, Battisti et al. [53] performed MD simulations with a rigid framework of ZIF-7 and could not measure diffusion for any gas adsorbed in ZIF-7, which is in contradiction with the results obtained including framework flexibility, as well as with recent experiments on the same material [54]. Flexibility is not a major issue if the kinetic size of the gas molecule is smaller than the pore size of the material. Therefore, we only compared simulation results for H_2 permeances through ZIF-8 membranes since H_2 is a smaller molecule compared to pores of ZIF-8 (2.96 Å). There is a good agreement between experimental measurements of different research groups and our simulation studies as shown in Figure 6. The simulation data of large gases (CH_4 and N_2) are not included since our simulations used ZIF-8 as rigid. Density functional theory (DFT) calculations are appropriate to evaluate permeance properties of flexible MOFs at different

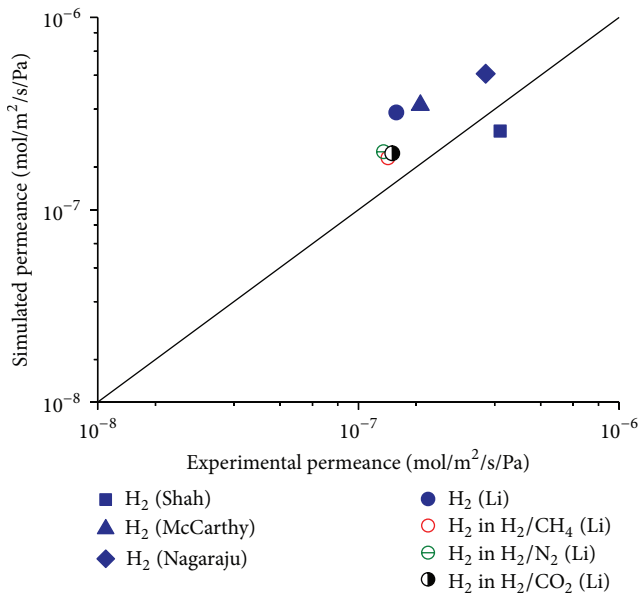

Figure 6: Comparison of our molecular simulations and experiments for single-component and mixture permeances through ZIF-8 membrane.

structural configurations. These calculations are computationally demanding and must be applied if a material is shown to exhibit framework flexibility by experiments. The aim of our computational approach is to predict gas permeance properties of MOF membranes on time scales shorter than the same materials that can be assessed experimentally.

4. Conclusions

In this work, we demonstrated a computational approach that combines GCMC and EMD simulations to predict membrane properties of MOFs. The enormous number of MOF materials provides a challenge for identifying the highly promising materials as membranes. In order to screen large number of MOFs for a given gas separation application, computational approaches should be used prior to extensive experimental efforts. We described a methodology that accurately predicts gas permeances of MOF membranes based on the results of GCMC and EMD simulations. Comparison of our simulation results with the experimentally measured gas permeances data for eight different MOF membranes showed that there is a good agreement between measured and simulated gas permeances data for both pure gases and gas mixtures. The only experimental input to compute these simulations is the XRD structures of MOFs. Therefore, molecular simulations can be performed for any MOF that has an XRD data. This computational approach will be highly useful to make accurate predictions about the gas separation properties of MOF membranes in a time-efficient manner.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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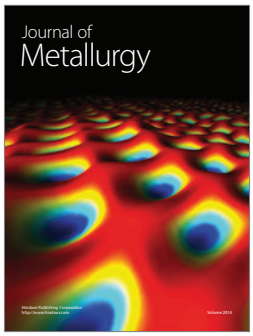

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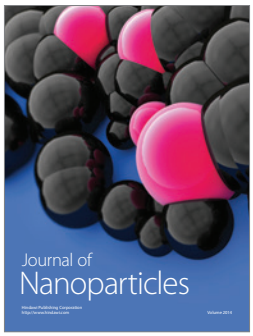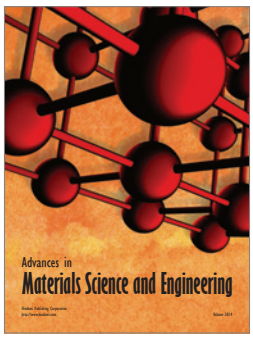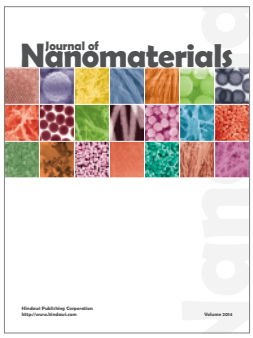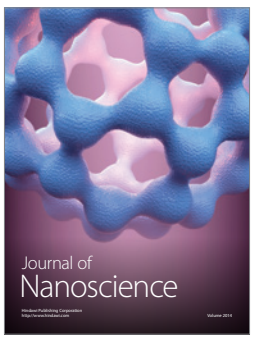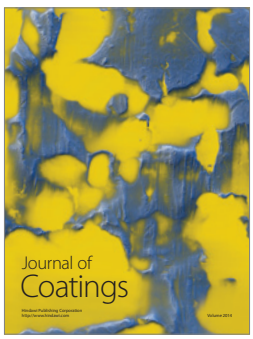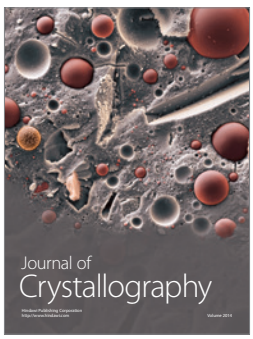
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