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Molecular Simulations for Adsorption-Based CO$_2$ Separation Using Metal Organic Frameworks

Seda Keskin

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Abstract

Metal organic frameworks (MOFs) have received significant attention as a new family of nanoporous materials in the last decade. Variations in geometry, size, and chemical functionality of these materials have led to several thousands of different MOF structures. MOFs typically have high porosities, large surface areas, and reasonable thermal and mechanical stabilities. These properties make them ideal adsorbents for adsorption-based gas separations. It is not practically possible to test the adsorption-based gas separation potential of all available MOFs using purely experimental techniques. Molecular simulations can guide experimental studies by providing insights into the gas adsorption and separation mechanisms of MOFs. Several molecular simulation studies have examined adsorption-based CO$_2$ separation using MOFs due to the importance of CO$_2$ capture for clean energy applications. These simulations have been able to identify the MOF having the most promising CO$_2$ separation properties prior to extensive experimental efforts. The aim of this chapter is to address current opportunities and challenges of molecular simulations of MOFs for adsorption-based CO$_2$ separations and to provide an outlook for prospective simulation studies.

Keywords: MOF, molecular simulation, adsorption, separation

1. Introduction

We have witnessed the quick growth of a new group of nanoporous materials named as metal organic frameworks (MOFs) in the last decade. MOFs are crystalline nanoporous materials composed of metal complexes that are linked by organic ligands to create highly porous frameworks [1, 2]. MOFs become strong alternatives to more traditional nanoporous materials such as zeolites due to their fascinating physical and chemical properties. MOFs

typically have very large surface areas (500–6000 m^2/g), high pore volumes (1–4 cm^3/g), wide range of pore sizes from micro- to mesoscale (1–98 Å), and reasonable thermal and mechanical stabilities. The most important characteristic of MOFs is that their physical, chemical, and structural properties can be tuned during synthesis. This controllable synthesis leads to a large diversity of materials having different geometry, pore size, and chemical functionality [3, 4]. As a result, thousands of MOFs have been reported in the Cambridge Crystallographic Database [5]. The family of MOFs can be divided into subgroups such as isoreticular MOFs (IRMOFs), zeolitic imidazolate frameworks (ZIFs), zeolite-like MOFs (ZMOFs), and covalent organic frameworks (COFs).

MOFs have been examined for a variety of chemical applications including gas storage [6, 7], gas sensing [8], gas separating membranes [9], mixed matrix membranes [10], catalysis [11], and biomedical applications [12, 13]. Among these applications, gas separation has received a significant interest because the pore sizes of MOFs can be tuned to selectively separate gases at the molecular level. Gas separation using MOFs has been generally studied in two categories: equilibrium-based gas separations and kinetic-based gas separations [14]. In equilibrium-based gas separations, MOFs are used as adsorbents and in kinetic-based separations, MOFs are used as membranes. Adsorption-based gas separation is governed by the thermodynamic equilibrium. Gas components are reversibly adsorbed into the pores of the adsorbent. An ideal adsorbent material must have a good combination of adsorption selectivity and working capacity in addition to high stability, high void volume, and well-defined pore sizes. High porosities, large surface areas, different pore sizes and shapes, and reasonable stabilities of MOFs suggest that these materials can be ideal adsorbents in equilibrium-based gas separation applications. Several experimental studies have been carried out for adsorption-based gas separations using MOFs [15–17].

Two criteria are widely investigated to assess the potential of MOF adsorbents: adsorption selectivity and working capacity. Adsorption selectivity is determined by the adsorption affinity of the MOF for one gas species relative to another. High adsorption selectivity means a high-purity product and hence lower energy requirements. Working capacity is defined as the difference between the adsorbed amounts of gas at the adsorption and desorption pressures. High working capacity means easy regeneration of the adsorbent material. For an efficient and economic adsorption-based gas separation, both high selectivity and high working capacity are desired. Therefore, experimental studies on MOF adsorbents generally examine selectivity and working capacity of the materials [18].

Most of the experimental studies have focused on CO_2 separation. Because of the growing environmental concerns, removal of CO_2 from natural gas (CO_2/CH_4), flue gas (CO_2/N_2), and other gases (CO_2/H_2) becomes an important issue. Experimentally measured selectivity and gas uptake capacity of several MOFs for separation of CO_2 from CH_4 and N_2 have been summarized in the literature [19]. Currently available adsorbents such as activated carbons, carbon molecular sieves, and zeolites are not highly selective for CO_2 separation, especially for separation of CO_2 from flue gas [20]. A good comparison of CO_2 separation performances of different nanoporous materials such as MOFs, zeolites, and activated carbons is available in a recent review [21]. It is shown that CO_2/N_2 selectivity changes from low in zeolites to moderate

in carbon-based absorbents and becomes high in MOFs. Therefore, research on adsorption-based gas separations has focused on identifying highly selective MOF adsorbents with high CO$_2$ capacities that can replace traditional adsorbents.

Considering the very large number of available MOFs, it is not possible to test thousands of different MOFs as adsorbents using purely experimental methods. Molecular simulations play an increasingly important role in understanding the potential of MOFs in adsorption-based gas separations. Among molecular simulation methods, grand canonical Monte Carlo (GCMC) simulations have been widely used to accurately predict adsorption isotherms of various gases in MOFs [22]. Gas selectivities calculated from simulated adsorption isotherms are generally found to be in good agreement with the experiments [23]. In most studies, single-component gas adsorption isotherms are computed using GCMC simulations; mixture adsorption isotherms are then predicted based on pure gas adsorption data using ideal adsorbed solution theory (IAST). IAST is a well-developed technique to describe adsorption equilibria for gas components in a mixture using only single-component adsorption data at the same temperature and on the same adsorbent [24]. GCMC simulations can be also performed to obtain mixture adsorption data directly. This data is then used to predict adsorption selectivity and working capacity of the MOF. Results of molecular simulations provide molecular-level insights which can be used to design new MOFs with better separation performances. In the early years of these studies, simulations examined only one or a few MOFs at a time. With the development of new computational approaches and with the quick increase in the number of synthesized MOFs, molecular simulations have started to screen a large numbers of materials. The results of large-scale MOF screening studies are highly useful to direct experimental efforts, resources, and time to the most promising MOF materials.

This chapter aims to address the importance of molecular simulations to evaluate the potential of MOFs in adsorption-based CO$_2$ separations. Section 2.1 introduces details of GCMC simulations to study CO$_2$ adsorption in MOFs. Section 2.2 describes evaluation criteria used to assess CO$_2$ separation potential of MOF adsorbents. Studies on large-scale computational screening of MOF adsorbents are discussed in Section 2.3. Structure-separation performance relations obtained from molecular simulations of MOFs are summarized in Section 2.4. Section 3 closes by addressing the opportunities of using molecular simulations for examining the potential of MOF adsorbents in CO$_2$ separations.

2. Molecular simulations for CO$_2$ separation using MOFs

2.1. GCMC simulations for CO$_2$ adsorption

GCMC is a well-known method to estimate the adsorption equilibria of gases in nanoporous materials. This simulation mainly mimics an adsorption experiment. In an experimental setup, the adsorbed gas is in equilibrium with the gas in the reservoir at fixed temperature, volume, and chemical potential [25]. GCMC simulations are run at an ensemble where the temperature, volume, and chemical potential are kept constant and the number of gas molecules is allowed to fluctuate during the simulation at the imposed temperature and chemical potential. The

output of a GCMC simulation is the number of adsorbed gas molecules per unit cell of the MOF structure at predetermined temperature and pressure. These simulations provide single-component adsorption isotherms, binary mixture adsorption isotherms, and isosteric heat of adsorptions which are directly comparable with the output of adsorption experiments. In GCMC simulations where only a single-component gas such as CO_2 is studied, four different types of moves are considered including translation, rotation, insertion, and deletion of a molecule. In mixture GCMC simulations where a binary gas mixture is considered such as CO_2/H_2, CO_2/CH_4, and CO_2/N_2, another trial move, exchange of molecules is also performed in order to speed up the equilibrium. The adsorbed amounts of each gas component are calculated by specifying pressure, temperature, and composition of the bulk gas mixture in GCMC simulations.

In a typical GCMC simulation of CO_2 adsorption in an MOF, CO_2 is the adsorbate and MOF is the adsorbent. Adsorbate molecules interact with the MOF atoms and with other adsorbates through dispersive and electrostatic interactions. These interactions are defined using a force field. A force field is the functional form and parameter sets are used to calculate the potential energy of a system of atoms in molecular simulations [26]. There are several potentials such as Lennard-Jones (LJ) [27] and Morse [28] potentials. In almost all molecular simulations of gases in MOFs, Lennard-Jones (LJ) potential is used. Results of a GCMC simulation may vary depending on the force field choice. General-purpose force fields such as universal force field (UFF) [29] and DREIDING force field [30] have been widely employed for simulations of MOFs. At the early stages of the molecular simulation studies of MOFs, efforts have been made to develop new force fields specific to MOF-gas interactions using quantum-level calculations [31, 32]. Some studies refined the force field parameters to match the predictions of molecular simulations with the available experimental measurements of gas adsorption in MOFs [32–36]. However, considering the large number and variety of MOFs, it is challenging to develop a new force field or refine an existing one for every single MOF. Therefore, generic force fields such as UFF and DREIDING are mostly preferred in molecular simulations of CO_2 adsorption in MOFs, especially for large-scale computational screening of MOFs. The reliability of the molecular simulation studies, of course, hinges on the accuracy of the force fields used. Schmidt et al. [37] computed CO_2 adsorption isotherms in a very large number of MOFs using ab initio force fields to probe the accuracy of common force fields. They concluded that there are significant quantitative differences between gas uptakes predicted by generic force fields such as UFF and ab initio force fields, but the force fields predict similar ranking of the MOFs, supporting the further use of generic force fields in large-scale material screening studies.

The LJ potential parameters of CO_2 are generally taken from the force field developed by Potoff and Siepmann [38]. A rigid linear triatomic molecule with three charged LJ interaction sites located at each atom is used for CO_2 molecules. Partial point charges centered at each LJ site approximately represent the first-order electrostatic and second-order induction interactions. Charge-quadrupole interactions between MOF atoms and CO_2 molecules significantly contribute to the adsorption of CO_2. It was shown that if these interactions are not taken into account, adsorption isotherms of CO_2 molecules in MOFs can be significantly underestimated [39]. In order to compute the electrostatic interactions between CO_2 molecules and MOF, partial

point charges must be assigned to the MOF atoms. Several different methods are available in the literature to assign partial charges such as density-derived electrostatic and chemical charge (DDEC) method [40], connectivity-based atom contribution (CBAC) method [41], extended charge equilibration (EQeq) method [42], and quantum mechanical methods based on the ChelpG [43] density functional theory (DFT) calculations. Charges obtained from different methods generally do not agree well with each other. This is acceptable because atomic charges are not experimentally observable and the methods used to derive them depend on the physical phenomenon the charges are intended to be reproduced [44]. A simulated CO_2 adsorption isotherm is generally compared with the experimentally measured one to tune the charges if necessary. After atomic models, force fields and charges are defined for CO_2 molecules and MOF atoms, GCMC simulations can be carried out to obtain the adsorbed gas amounts. Results of these simulations are directly used to calculate the adsorption-based gas separation potential of MOFs based on several criteria as discussed below.

2.2. Evaluation of MOF adsorbents for CO_2 separation

In adsorption-based gas separation processes such as pressure swing adsorption (PSA), selectivity and working capacity of the adsorbent are the two important parameters that define the efficiency of the process [45, 46]. Adsorption selectivity is described as the ratio of mole fractions of gases in the adsorbed phase normalized by the bulk composition of the gas mixture:

$$S_{ads(1/2)} = \frac{x_1/x_2}{y_1/y_2}$$

(1)

Here, x stands for the molar fraction of the adsorbed phase obtained from the GCMC simulations, while y represents the molar fraction of the bulk gas phase. Eq. (1) defines the adsorption selectivity of an MOF adsorbent with respect to component 1, meaning that if selectivity is greater than 1, then the adsorbent is selective for component 1 over 2. Selectivities for CO_2/CH_4, CO_2/H_2, and CO_2/N_2 mixtures are calculated using the results of binary mixture GCMC simulations where 1 is CO_2 and 2 is the other gas component in Eq. (1). The bulk gas compositions of CO_2/CH_4, CO_2/H_2, and CO_2/N_2 mixtures are generally set to 50/50, 15/85, and 15/85, respectively, in molecular simulations to represent industrial operating conditions.

Working capacity (ΔN) is described as the difference between the loading amounts of the strongly adsorbed gas at the corresponding adsorption (N^{ads}) and desorption (N^{des}) pressures [46]. It is defined in the unit of mol gas per kg of MOF adsorbent. GCMC simulations are performed at specific adsorption and desorption pressures to calculate the working capacity as shown in Eq. (2).

$$\Delta N_1 = N_1^{ads} - N_1^{des}$$

(2)

Bae and Snurr [45] recently suggested some other adsorbent evaluation criteria in addition to selectivity and working capacity. The CO_2 uptake of an MOF under adsorption conditions

(N^{des}), sorbent selection parameter (S_{sp}), and regenerability ($R\%$) are also considered as adsorbent evaluation criteria to assess the potentials of MOFs in CO_2 separation processes such as natural gas purification, landfill gas separation, and CO_2 capture from power-plant flue gas. The CO_2 uptake of an MOF under adsorption conditions (N^{ads}) is the direct output of GCMC simulations. Sorbent selection parameter (S_{sp}) is defined as the combination of adsorption selectivity and working capacity. It is used to compare performances of different nanoporous materials in adsorption-based separation processes and is defined as shown in Eq. (3). Here, subscripts 1 and 2 indicate the strongly adsorbed component and the weakly adsorbed component, respectively. In CO_2-related mixtures, CO_2 is generally the strongly adsorbed component (1), whereas other gases such as CH_4 and N_2 are weakly adsorbed (2).

$$S_{sp} = \frac{(S_{ads(1/2)})^2}{S_{des(1/2)}} \times \frac{\Delta N_1}{\Delta N_2} \tag{3}$$

Regenerability ($R\%$) is defined as the ratio of working capacity to the amount of the adsorbed gas at the adsorption pressure and it is an important parameter to evaluate the practical usage of an adsorbent for cyclic PSA and vacuum swing adsorption (VSA) processes:

$$R(\%) = \frac{\Delta N_1}{N_1^{ads}} \times 100 \tag{4}$$

At that point, it is important to mention that none of these criteria are perfect but they are complementary with each other to assess adsorbent potential of MOFs under practical conditions. Bae and Snurr [45] calculated adsorption selectivity, working capacity, gas uptake capacity, sorbent selection parameter, and regenerability values of several MOFs for adsorption-based separation of CO_2/CH_4:10/90, CO_2/CH_4:50/50, and CO_2/N_2:10/90 mixtures. Although mixtures are considered, they used the experimental single-component adsorption isotherm data from the literature and obtained mixture amounts under adsorption and desorption conditions at the partial pressure of the specific component. In order to investigate the effect of mixture data, Ozturk and Keskin [47] calculated the same separation properties of MOFs using both single-component and mixture GCMC data. They showed that selectivity calculated from single-component GCMC simulations can be enormously different than the selectivity calculated from mixture GCMC simulations due to strong competition effects between different gas species. Therefore, it is better to characterize adsorbent materials based on their performance for mixed-gas feeds to reflect the real operation conditions [48].

Llewellyn et al. [49] recently suggested a new criterion named as adsorbent performance indicator (API) as shown in Eq. (5) to initially highlight porous materials of potential interest for PSA processes. This indicator takes into account working capacity (represented as WC in Eq. (5)), adsorption energy ($\Delta H_{ads,1}$) of the most adsorbed species, and selectivity (S_{ads}). It additionally uses weighting factors to reflect the specific requirements of a given process.

$$API = \frac{(S_{ads(1/2)}-1)^A \times WC_1^B}{|\Delta H_{ads,1}|^C} \qquad (5)$$

They calculated APIs of seven MOFs for two different CO_2/CH_4 separation scenarios using the experimental gas adsorption data [49]. Results showed that API can be more versatile than previously discussed comparison criteria for an initial indication of potential adsorbent performance.

2.3. Performance of MOFs in CO_2 separations

It is beyond the scope of this chapter to give a complete account of all GCMC studies of MOFs for CO_2 separation. Several molecular simulation studies examined a single MOF or a few MOFs at a time [50–59]. Most of these studies focused on adsorption-based separation of CO_2 using the two most widely studied MOFs, MOF-5 and CuBTC [60–64]. This section will focus on molecular simulation studies that examine a family of MOFs for adsorption-based CO_2 separations and large-scale computational screening studies to provide a relation between structure and separation performance of MOFs.

2.3.1. IRMOFs

IRMOFs are isoreticular MOFs. The "IR" stands for isoreticular, which essentially means that the molecular system is "stitched together" into a netlike structure through strong chemical bonds. Molecular simulations were used to compare the separation of CO_2/N_2 mixtures in two different classes of nanoporous materials, traditional zeolites (MFI, LTA, and DDR) and MOFs (IRMOF-1, -11, -12, -13, -14, CuBTC, and MIL-47 (V)) [65]. Results showed that although MOFs perform much better for gas storage than zeolites, their CO_2 separation performance is comparable to zeolites with adsorption selectivities in the range of 5–35. Krishna and van Baten [46] used configurational-bias Monte Carlo (CBMC) simulations to examine zeolites and IRMOF-1, MOF-177, rho-ZMOF, CuBTC, ZnMOF-74, and MgMOF-74 for separation of CO_2/CH_4, CO_2/N_2, and CO_2/H_2 mixtures using PSA units. The best CO_2 capture performance was obtained with MgMOF-74 that offers strong electrostatic interactions of CO_2 molecules with the exposed metal cation sites. Selectivity of MgMOF-74 was reported as ~300, 50, and 10 for CO_2/H_2, CO_2/N_2, and CO_2/CH_4 separations, respectively. Traditional zeolite adsorbents such as NaX and NaY show higher adsorption selectivities for these gas separations but these two zeolites suffer from relatively low working capacities that are important in PSA units. For CO_2/N_2 and CO_2/H_2 separation in PSA units, MgMOF-74 was found to offer the best combination of high adsorption selectivity and high working capacity. Han et al. [66] used GCMC simulations with first-principles-based force fields to report the effects of interpenetration on the CO_2/H_2 separation of MOFs. Non-interpenetrating IRMOF-1, -7, -8, -10, -14, -16, MOF-177, and MOF-200 and interpenetrating IRMOF-9, -13, -62, and SUMOF-4 were considered for comparison. For example, IRMOF-9 and IRMOF-13 are interpenetrating versions of IRMOF-10 and -14, respectively. The interpenetration of MOFs at low pressure remarkably enhanced the selectivity of CO_2 over H_2 by creating new adsorption sites for CO_2. However, selectivity of

the interpenetrating and non-interpenetrating MOFs was reversed at higher pressures. Since interpenetration lowers the pore volume of MOFs, it significantly reduced CO_2 uptake at high pressures. The decrease in the H_2 uptake resulting from interpenetration was found to be marginal. Therefore, selectivity of the interpenetrating MOFs was reported to be lower than that of non-interpenetrating MOFs at high pressures.

2.3.2. ZIFs

Zeolitic imidazolate frameworks (ZIFs) are composed of tetrahedral networks that resemble those of zeolites with transition metals connected by imidazolate ligands. Zeolites are known with the $Al(Si)O_2$ unit formula, whereas ZIFs are recognized by $M(Im)_2$, where M is the transition metal and Im is the imidazolate-type linker. Battisti et al. [67] calculated CO_2/CH_4, CO_2/H_2, and CO_2/N_2 adsorption selectivity in the zero-pressure limit for nine ZIFs, ZIF-2, -3, -4, -5, -6, -7, -8, -9, and -10 using GCMC simulations. These ZIFs were characterized by pores

Figure 1. Adsorption-based separation performance of ZIFs for (a) CH_4/H_2, (b) CO_2/CH_4, and (c) CO_2/H_2 mixtures. The compositions of the bulk gas mixtures are (a) 10/90, (b) 10/90, and (c) 1/99 for ZIFs at 298 K and (a) 50/50, (b) 50/50, and (c) 15/85 for zeolites at 300 K. Reprinted with permission from Ref. [68]. Copyright (2012) American Chemical Society.

of medium to small size compared to other MOFs. Therefore, they were able to store at most half of the amount of gases than other MOFs. ZIF-7 and ZIF-9 were shown to be promising due to their high adsorption selectivities of 280 and 15 for CO_2/H_2 and CO_2/N_2 separations, respectively. Atci and Keskin [68] used GCMC simulations to predict the performance of 15 different ZIFs (ZIF-1, -2, -3, -6, -8, -10, -60, -65, -67, -68, -69, -70, -79, -81, and -90) in both adsorption-based and membrane-based separations of CH_4/H_2, CO_2/CH_4, and CO_2/H_2 mixtures. Adsorption selectivity, working capacity, membrane selectivity, and gas permeability of ZIFs were predicted using GCMC and molecular dynamics simulations. **Figure 1** compares adsorption selectivities and working capacities (shown as delta loadings) of ZIFs calculated at an adsorption pressure of 10 bar and desorption pressure of 1 bar with the data for zeolites and MOFs [68]. Several ZIFs were identified to outperform traditional zeolites and widely studied MOFs in CO_2/CH_4 and CO_2/H_2 separations. Keskin's group [69] also calculated adsorption of both single-component gases (CH_4, CO_2, H_2, and N_2) and binary gas mixtures (CO_2/CH_4, CO_2/N_2, and CO_2/H_2) using GCMC simulations and predicted the ideal and mixture adsorption selectivities of ZIFs. They showed that the adsorption selectivity calculated from mixture GCMC simulations can be significantly higher than the ideal adsorption selectivity calculated from single-component adsorption isotherms. This result highlighted the importance of using mixture selectivity to assess the performance of MOF adsorbents.

The calculated adsorption selectivity of ZIFs may vary significantly depending on the force field parameters used in molecular simulations [70]. Generic force fields generally tend to overestimate gas adsorption capacities; hence, adsorption selectivities of ZIF-68 and ZIF-69 compared to the tailored-force fields. However, the difference between predicted adsorption selectivities of different force fields is not high enough to change the assessment about the separation performance of the material. Both generic and tailored-force fields were able to identify the promising adsorbent materials that exhibit high adsorption selectivities. In other words, generic force fields can be safely used to screen large number of MOFs to differentiate between the promising and non-promising materials.

2.3.3. PCNs

MOFs are also referred as porous coordination networks (PCNs) in the literature and several synthesized materials have been named as PCNs [71]. Ozturk and Keskin [72] studied 20 different PCNs (PCN-6, 6', 9-Co, 9-Mn, 9-Fe, 10, 11, 13, 14, 16, 16', 18, 19, 20, 26, 39, 46, 80, 131', and 224-Ni) using molecular simulations to identify the most promising adsorbent and membrane candidates for CO_2/H_2, CO_2/CH_4, and CO_2/N_2 mixtures. PCN-9-Co, -9-Mn, -14, and -16 were found to be strong adsorbents for CO_2 capture, especially for CO_2/CH_4 separations because of their high working capacities. They also developed a simple model that can predict adsorption selectivities of PCNs for CO_2/H_2 mixtures without performing extensive molecular simulations. The model was based on the structural and chemical properties of the materials that can be simply measured or computed, such as pore volume, surface area, and the inverse of difference of heat of adsorption of components in the mixture. Predictions of the model for adsorbent selectivities were found to be in good agreement with the direct results of detailed molecular simulations.

2.3.4. COFs

Covalent organic frameworks (COFs) are not strictly MOFs but similar materials. They are formed by building units linked into a periodic framework but in contrast to MOFs, all components are organic in COFs. Zhong's group [73] examined a diverse set of 46 COFs to predict their separation performance for industrial gas mixtures, CO_2/H_2 and CO_2/CH_4, using PSA process. Results show that COFs outperform most commonly used zeolites and widely studied MOFs in the separation of CH_4/H_2 while they have a comparable performance in separating CO_2/H_2 and CO_2/CH_4. The same group then studied the performance of 151 MOFs with large chemical and topological diversity for CO_2/CH_4 separation for temperature swing adsorption (TSA) process [74]. The thermal regeneration energy was used as an evaluation criterion in addition to adsorption selectivity, working capacity, and regenerability. Cu-TDPAT and IRMOF-1-2Li MOFs were reported as the most promising candidates for CO_2/CH_4 separation in TSA processes based on the ranking of the materials according to the four evaluation criteria. Cu-TDPAT was identified as the best adsorbent candidate because of its high thermal stability and water-stable property.

2.3.5. Large-scale screening of MOFs

In 2012, Sholl's group [75] used GCMC simulations to calculate adsorption of CO_2 and N_2 in 500 different MOFs. This was the largest set of structures for which this information has been reported until 2012. Adsorption selectivities of MOFs were calculated using Henry's constant at infinite dilute loading. More detailed calculations such as quantum chemistry methods and binary mixture GCMC simulations were then carried out to assess adsorption selectivities of highly promising MOFs. Watanabe and Sholl [76] later on screened a larger number of MOFs for CO_2/N_2 separation. They first analyzed pore characteristics of 1163 MOFs using a simple steric model developed by Haldoupis et al. [77]. Adsorption selectivity of the selected 201 MOFs was calculated using single-component GCMC simulations at infinite dilute loading. Selectivities were plotted as a function of largest cavity diameter (LCD) of MOFs as shown in **Figure 2**. This figure demonstrates that MOFs are promising materials for CO_2/N_2 separations. There is a significant number of MOFs with high selectivities of 100–1000. A small number of materials have extremely high adsorption selectivities, greater than 1000. Selectivities of the top 10 promising MOFs were also computed considering CO_2/N_2:15/85 mixture and results showed that CO_2/N_2 selectivities of MOFs remained high even for binary gas mixtures with the composition of dry flue gas.

Lin et al. [78] screened hundreds of thousands of hypothetical zeolite and ZIF structures for CO_2 capture from flue gas. They determined the optimal process conditions of each material by minimizing the electric load imposed on a power plant by a temperature-pressure swing capture process using that material followed by compression. This minimum load was called as parasitic energy and it was introduced as a metric to compare different materials. Results of that study showed that parasitic energy for ZIFs is higher than for zeolites. Wilmer et al. [79] drastically expanded the scope of previous MOF screening studies by examining over 130,000 hypothetical MOFs. They used molecular simulation to calculate adsorption selectivity, working capacity, regenerability, and sorbent selection parameter of MOFs for CO_2/CH_4 and

CO_2/N_2 separations. Single-component GCMC simulations to obtain the pure component CO_2, CH_4, and N_2 adsorption data are required to calculate the five adsorbent evaluation criteria. The resulting simulation data exhibited sharply defined structure-property relationships as we will discuss in Section 2.4. These type of relationships were not apparent when smaller collections of MOFs were studied in the previous works, indicating that screening large number of MOFs is important to understand the effect of structure on the gas separation performance of MOFs.

Figure 2. CO_2/N_2 sorption selectivity of the MOFs at 303 K. The data include only the materials with CO_2 diffusivity greater than 10^{-8} cm^2/s. Reprinted with permission from Ref. [76]. Copyright (2012) American Chemical Society.

2.3.6. Breakthrough calculations

We so far discussed the molecular simulation studies in the literature that mimic a classical adsorption experiment. Other than isotherm experiments, breakthrough experiments are also carried out on nanoporous adsorbents in order to investigate the materials' kinetics. However, these experiments are labor-intensive and can present a range of technical challenges to achieve accurate results. Krishna and Long [80] suggested a new metric, breakthrough time (τ_{break}), that is based on the analysis of the transient response of an adsorber to a step input of a gaseous mixture. This metric determines the frequency of required regeneration of an adsorbent. High value of τ_{break} is desirable in practice because it reduces the frequency of required regeneration. Breakthrough calculations were done for separation of CO_2/H_2, CO_2/CH_4, and $CO_2/CH_4/H_2$ mixtures using five MOFs, MgMOF-74, CuBTTri, MOF-177, BeBTB, and Co(BDP) and results were compared with traditional zeolites. MgMOF-74 emerged as the best material from the viewpoints of both frequency of regeneration and productivity. The advantage of MgMOF-74 over traditionally used NaX zeolite was found to be evident at pressures exceeding 10 bar.

Krishna and van Baten [81] later studied breakthrough characteristics of an adsorber packed with a number of zeolites (MFI, JBW, AFX, and NaX) and MOFs (MgMOF-74, MOF-177, and CuBTTri-mmen) for CO_2 capture from a CO_2/N_2 mixture. These calculations demonstrated that high capacities could have a dominant influence on the overall performance of PSA units. MgMOF-74 was again identified as a promising adsorbent with a CO_2 capture capacity more than twice that of other materials investigated. For separation of CO_2/H_2, CO_2/CH_4, and CH_4/H_2 mixtures, Jiang's group [82] recently studied seven different *rht*-MOFs namely Cu-TDPAT, PCN-61,-66,-68, NOTT-112, NU-111, and NU-110. These MOFs have the same *rht* topology with different ligands. The breakthrough profiles for CO_2-containing mixtures were predicted from the simulation results. Due to the presence of small ligands, unsaturated metals, and amine groups, Cu-TDPAT was found to exhibit the highest adsorption capacity and separation performance among the seven *rht*-MOFs. Upon substituting the phenyl rings in Cu-TDPAT by pyridine rings, Cu-TDPAT-N was designed and the breakthrough time for CO_2 in Cu-TDPAT-N was found to be extended by twofold. This result shows the importance of understanding structure-separation performance relations for MOFs as we discuss below.

2.4. Structure-performance relations

High-throughput computational screening is a very useful approach to identify promising MOF materials for gas separation applications and to uncover structure-property relations [83]. With the development of new computational methodologies, it is now easier to perform large-scale computational screening studies where the properties of thousands of MOF candidates can be evaluated and compared. When this type of large-scale MOF screening is performed, a large amount of data is produced and used to investigate correlations between MOFs' structural properties and their gas separation performances.
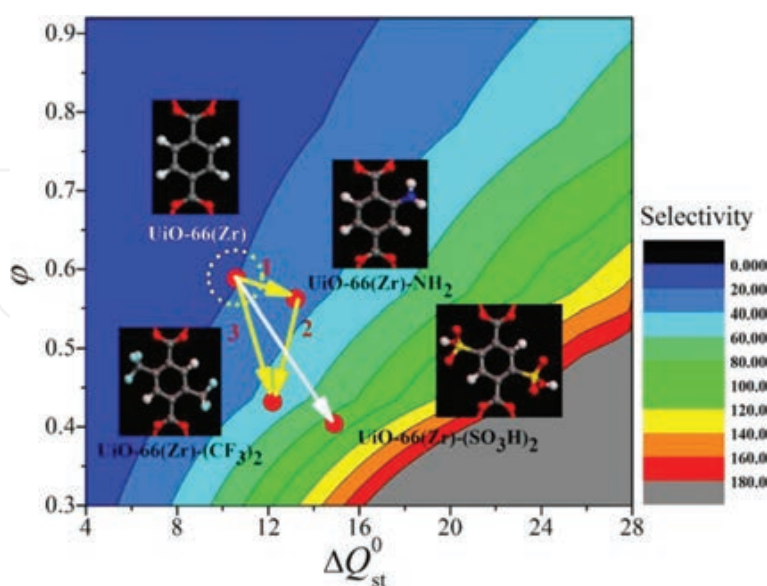

Figure 3. The interplay map of ϕ and ΔQ_{st}^0 on their impact on the selectivity at 1 bar for CO_2/N_2 mixture in MOFs, where the design strategy based on UiO-66(Zr) is also given. Reprinted with permission from Ref. [84]. Copyright (2012) American Chemical Society.

Maurin's group [84] used molecular simulations to examine separation performance of 105 MOFs with a large chemical and topological diversity for CO$_2$ capture from flue gas under industrial operating conditions. They developed a quantitative structure-property relationship (QSPR) model from this extended series of MOFs to rationalize the resulting CO$_2$/N$_2$ selectivity. The difference of isosteric heats of adsorption between CO$_2$ and N$_2$ at infinite dilution (ΔQ_{st}^0) and porosity (ϕ) were found to be the main features of the MOFs that strongly impact the CO$_2$/N$_2$ adsorption selectivity at 1 bar. **Figure 3** shows the interplay map of these two factors on the calculated CO$_2$/N$_2$ adsorption selectivity. Results of QSPR analysis suggested that increasing ΔQ_{st}^0 and simultaneously decreasing ϕ seems to be an appropriate route to enhance the CO$_2$/N$_2$ selectivity of MOFs. Motivated from this structure-performance relation, a new functionalized MOF, UiO-66(Zr)-(SO$_3$H)$_2$, was computationally designed and predicted to exhibit a high CO$_2$/N$_2$ selectivity as shown in **Figure 3**.

The CO$_2$ separation potential of a new class of porous aromatic frameworks (PAFs) with diamond-like structure was studied by molecular simulations [85]. It was discussed that selectivity might be only determined by the difference of the gas-material interactions of the mixtures at a pressure close to zero. The CO$_2$/H$_2$, CO$_2$/N$_2$, and CO$_2$/CH$_4$ selectivities and the difference of isosteric heats (ΔQ_{st}^0) were calculated at the pressure close to zero. The ΔQ_{st}^0 was found to be linear with the logarithm of the selectivity no matter what the gas mixtures and materials were. This result suggested that at zero pressure the selectivity is only dependent on the values of ΔQ_{st}^0 and is independent of the type of the gases and the materials. With the increase of ΔQ_{st}^0, the selectivity increases correspondingly, which means that the ΔQ_{st}^0 can be used instead of the selectivity to screen out the promising nanoporous materials for gas separation. Finding a correlation between adsorption selectivity and ΔQ_{st}^0 is useful. However, it is difficult to design new MOF materials that have a priori chosen Q_{st} value. It is easier to design materials based on measurable structural properties such as porosity, pore size, or surface area. Wilmer et al. [79] studied a very large number of hypothetical MOFs and showed clear correlations between purely structural characteristics such as pore size, surface area, and pore volume as well as chemical characteristics such as functional groups with five adsorbent evaluation criteria listed in Section 2.2. For example, it was shown that adsorption selectivity correlates well with the maximum pore diameter for flue gas separation. Adsorption selectivity also correlates with the heat of adsorption of CO$_2$ for flue gas and natural gas separation. Certain chemical functional groups, particularly those with fluorine and chlorine atoms, were frequently found among the best performing MOF adsorbents. These type of structure-property relationships can be used as a guide for experimental MOF synthesis studies.

In a recent study, in silico screening of 4764 MOFs was performed for adsorption-based CO$_2$/CH$_4$ and CO$_2$/N$_2$ separations [86]. Quantitative relations between the metal type and adsorbent properties such as selectivity, working capacity, and regenerability were investigated for the first time in the literature. A wide variety of metals exists in MOFs such as alkalis, alkalines, lanthanides (Ln), and transition metals. **Figure 4** shows the probabilities of different metals in the selected MOFs based on their selectivity and working capacity for CO$_2$/CH$_4$ and CO$_2$/N$_2$ separations. For instance, the probability of K is about 0.8 for CO$_2$/N$_2$ separation, meaning that 80% of K-based MOFs show high selectivity and working capacity. Combining selectivity,

working capacity, and regenerability, however, alkali- and alkaline-MOFs possess the lowest performance for CO_2 separation. Among 4764 MOFs, about 1000 were found to contain Ln metals, 50% contain Ln as open metal sites. These open metal sites have high adsorption affinity for CO_2; therefore, MOFs with Ln metals have the highest CO_2 separation performance. The 30 best candidates identified for CO_2/CH_4 and CO_2/N_2 separations have Ln metals. These results can be used to synthesize MOFs having predetermined metal atoms to enhance the CO_2 separation performance of materials.
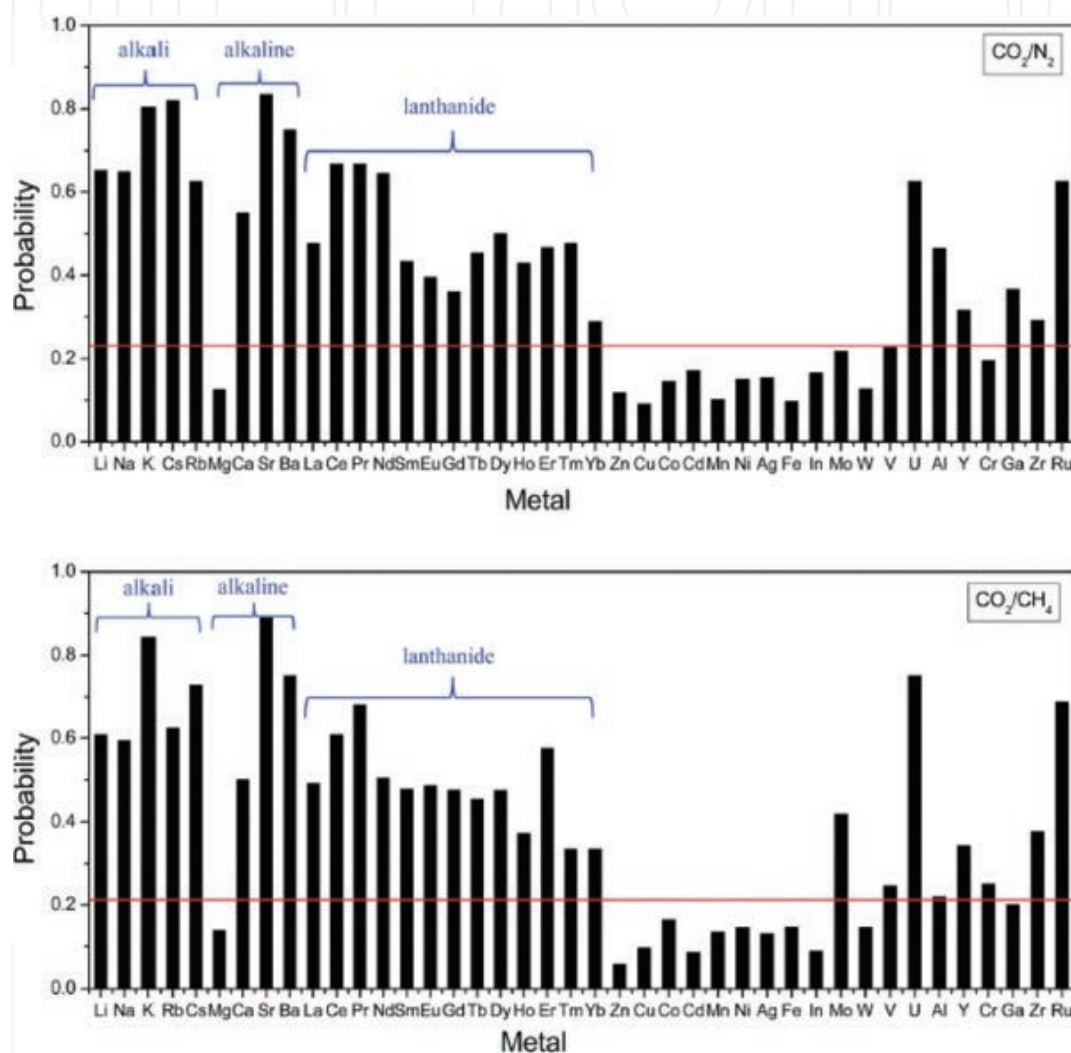

Figure 4. Probabilities of different metals in the selected MOFs (based on S and N_{CO2}). The red lines indicate the percentages of the selected MOFs from the total. Reprinted with permission from Ref. [84]. Copyright (2015) The Royal Society of Chemistry.

As can be seen from this literature review, current studies have generally focused on establishing relations between adsorption selectivity and a single chemical or structural property such as difference of isosteric heat of adsorption of gases or metal type. However, separation performances of materials are determined by the interplay of various factors and cannot be easily correlated to only one or two properties. All physical and chemical properties of MOFs including pore size, shape, porosity, surface area, topology, metal and organic linker type must

be considered to better understand structure-performance relations. Deriving structure-performance relations for MOFs is a new and developing research area and more studies in this area will be valuable to synthesize new MOFs with useful physical and chemical properties to achieve targeted gas separations.

3. Conclusion and outlook

Molecular simulations are very useful to quickly evaluate the potential of new MOF materials in adsorption-based gas separation processes. The outcome of molecular simulations can be used as a guide to design and develop new materials with enhanced separation properties. There is a continuous growth in the number of molecular simulation studies of MOFs for adsorption-based CO$_2$ separations. However, there are still several open areas in which future studies will be valuable. Opportunities and challenges related with these open research areas are discussed below:

3.1. Computational design of new materials

Strategies to improve the ability of MOFs to selectively adsorb CO$_2$ are reviewed in detail in the literature [87]. Some of these strategies are control of pore size, using materials with open metal sites, introduction of alkali-metal cations into MOFs, interpenetration, and using materials with polar functional groups [45, 88]. Among these, rational design of functionalized materials is a feasible way to improve the CO$_2$ separation efficiency of MOFs. GCMC simulations were recently used to study the effect of amine functionalization on the CO$_2$/CH$_4$ separation performance of MIL-53 [89]. Results showed that CO$_2$/CH$_4$ separation factor of − (NH$_2$)$_4$ amine-functionalized MIL-53 is the best and predicted separation performance of −NH$_2$ and −NHCO functionalized MIL-53 surpasses that of the original one. Future molecular simulation studies examining the effects of functionalization on the separation performance of MOFs will be very useful to establish guidelines for the experimental design and development of new materials.

3.2. Considering impurities in CO$_2$-related mixtures

As discussed in Section 2.3., most molecular simulation studies of MOFs focus on the separation of CO$_2$ from its binary mixtures such as CO$_2$/CH$_4$ and CO$_2$/N$_2$. However, in reality, these gas mixtures include some impurities. Water and the other minor components mostly H$_2$O, O$_2$, SO$_2$, and NOx cannot be ignored in assessing the performance of MOFs especially for post-combustion CO$_2$ capture. However, the number of molecular simulation studies examining the effects of trace gases on the CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation performance of MOFs is limited. Bahamon and Vega [90] recently used GCMC simulations to study 11 materials including zeolites and MOFs for separation of CO$_2$ from N$_2$, including water as an impurity. Sun et al. [91] studied 12 materials including MOFs, ZIFs, and zeolites for removal of SO$_2$ and NOx from flue gas using GCMC simulations. The influences of water and SO$_2$ on CO$_2$ adsorption and separation in UiO-66(Zr) MOFs with different functional groups were

evaluated using a combination of GCMC and DFT simulations [92]. Babarao et al. [93] considered small amounts of O_2, H_2O, and SO_2 impurities typically found in flue gas and evaluated the CO_2/N_2 selectivity of four PCNs in the presence of these impurities. Zhong's group [94] used molecular simulations to investigate the effect of trace amount of water on CO_2 capture in natural gas upgrading process in a diverse collection of 25 MOFs. These studies concluded that the effect of H_2O impurities on the CO_2 selectivity is highly specific to the chemistry of the framework and needs to be evaluated on an individual case-by-case basis. The CO_2 selectivity of MOFs was generally reported to decrease in the presence of water. Future studies on GCMC simulations of MOFs considering impurities in CO_2-related mixtures must be conducted to evaluate the potential use of MOFs in industrial CO_2 capture processes.

3.3. Multi-scale modeling

While CO_2 separation using MOF adsorbents has been extensively investigated in different MOFs, their performance under practical process conditions is scarcely examined. A multi-scale modeling study was recently carried out to examine CO_2 capture from flue gas by vacuum swing adsorption (VSA) process using *rho*-ZMOFs as adsorbents [95]. The full adsorption process was simulated and optimized and results showed that the operating spaces of *rho*-ZMOFs are similar to that of traditional 13X zeolite. Further studies that employ multi-scale modeling approaches will be useful to design and develop MOF-based industrial CO_2 separation processes. A related point is to test the long-term stability of MOF adsorbents under industrial operating conditions. An ideal MOF adsorbent must have good thermal and mechanical stability. Several MOFs are sensitive to atmospheric moisture and lose their crystal structures when exposed to water. This may be a significant problem when MOFs are used as adsorbents in flue gas separations since flue gas contains water. Molecular simulation studies that can provide information about the long-term stability of MOF adsorbents will be useful to evaluate the real performance of MOFs.

Author details

Seda Keskin

Address all correspondence to: skeskin@ku.edu.tr

Koc University, Chemical and Biological Engineering Department, Istanbul, Turkey

References

[1] Eddaoudi M, Li H, Yaghi O. Highly porous and stable metal-organic frameworks: structure design and sorption properties. Journal of the American Chemical Society. 2000;122:1391–1397. DOI: 10.1021/ja9933386

[2] Rowsell JL, Yaghi OM. Metal-organic frameworks: a new class of porous materials. Microporous and Mesoporous Materials. 2004;73:3–14. DOI: 10.1016/j.micromeso. 2004.03.034

[3] Farha OK, Hupp JT. Rational design, synthesis, purification, and activation of metal-organic framework materials. Accounts of Chemical Research. 2010;43:1166–1175. DOI: 10.1021/ar1000617

[4] Stock N, Biswas S. Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. Chemical Reviews. 2011;112:933–969. DOI: 10.1021/cr200304e

[5] Allen FH. The Cambridge structural database: a quarter of a million crystal structures and rising. Acta Crystallographica Section B: Structural Science. 2002;58:380–388. DOI: 10.1107/S0108768102003890

[6] Ren JW, Langmi HW, North BC, Mathe M. Review on processing of metal-organic framework (MOF) materials towards system integration for hydrogen storage. International Journal of Energy Research. 2015;39:607–620. DOI: 10.1002/er.3255

[7] Duan X, Wu CD, Xiang SC, Zhou W, Yildirim T, Cui YJ, et al. Novel microporous metal-organic framework exhibiting high acetylene and methane storage capacities. Inorganic Chemistry. 2015;54:4377–4381. DOI: 10.1021/acs.inorgchem.5b00194

[8] Li WJ, Gao SY, Liu TF, Han LW, Lin ZJ, Cao R. In situ growth of metal-organic framework thin films with gas sensing and molecule storage properties. Langmuir. 2013;29:8657–8664. DOI: 10.1021/la402012d

[9] Qiu SL, Xue M, Zhu GS. Metal-organic framework membranes: from synthesis to separation application. Chemical Society Reviews. 2014;43:6116–6140. DOI: 10.1039/c4cs00159a

[10] Zornoza B, Tellez C, Coronas J, Gascon J, Kapteijn F. Metal organic framework based mixed matrix membranes: an increasingly important field of research with a large application potential. Microporous and Mesoporous Materials. 2013;166:67–78. DOI: 10.1016/j.micromeso.2012.03.012

[11] Gascon J, Corma A, Kapteijn F, Xamena FXLI. Metal organic framework catalysis: Quo vadis? ACS Catalysis. 2014;4:361–378. DOI: 10.1021/cs400959k

[12] Della Rocca J, Liu DM, Lin WB. Nanoscale metal-organic frameworks for biomedical imaging and drug delivery. Accounts of Chemical Research. 2011;44:957–968. DOI: 10.1021/ar200028a

[13] Keskin S, Kizilel S. Biomedical applications of metal organic frameworks. Industrial & Engineering Chemistry Research. 2011;50:1799–1812. DOI: 10.1021/ie101312k

[14] Skoulidas AI, Sholl DS. Self-diffusion and transport diffusion of light gases in metal-organic framework materials assessed using molecular dynamics simulations. The Journal of Physical Chemistry B. 2005;109:15760–15768. DOI: 10.1021/jp051771y

[15] Liu J, Thallapally PK, McGrail BP, Brown DR, Liu J. Progress in adsorption-based CO_2 capture by metal-organic frameworks. Chemical Society Reviews. 2012;41:2308–2322. DOI: 10.1039/C1CS15221A

[16] Li J-R, Sculley J, Zhou H-C. Metal-organic frameworks for separations. Chemical Reviews. 2011;112:869–932. DOI: 10.1021/cr200190s

[17] Keskin S, van Heest TM, Sholl DS. Can metal-organic framework materials play a useful role in large-scale carbon dioxide separations? ChemSusChem. 2010;3;879-891. DOI: 10.1002/cssc.201000114

[18] Liu YY, Wang ZYU, Zhou HC. Recent advances in carbon dioxide capture with metal-organic frameworks. Greenhouse Gases-Science and Technology. 2012;2:239–259. DOI: 10.1002/ghg.1296

[19] Li JR, Ma YG, McCarthy MC, Sculley J, Yu JM, Jeong HK, et al. Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks. Coordination Chemistry Reviews. 2011;255:1791–1823. DOI: 10.1016/j.ccr.2011.02.012

[20] Aaron D, Tsouris C. Separation of CO_2 from flue gas: a review. Separation Science and Technology. 2005;40:321–348. DOI: 10.1081/Ss-200042244

[21] Ben-Mansour R, Habib MA, Bamidele OE, Basha M, Qasem NAA, Peedikakkal A, Laoui T, Ali M. Carbon capture by physical adsorption: materials, experimental investigations and numerical modeling and simulations – a review. Applied Energy. 2016;161:225–255. DOI: 10.1016/j.apenergy.2015.10.011

[22] Keskin S, Liu J, Rankin RB, Johnson JK, Sholl DS. Progress, opportunities, and challenges for applying atomically detailed modeling to molecular adsorption and transport in metal-organic framework materials. Industrial & Engineering Chemistry Research. 2009;48:2355–2371. DOI: 10.1021/Ie800666s

[23] Düren T, Bae YS, Snurr RQ. Using molecular simulation to characterise metal-organic frameworks for adsorption applications. Chemical Society Reviews. 2009;38:1237–1247. DOI: 10.1039/B803498M

[24] Myers AL, Prausnitz JM. Thermodynamics of mixed-gas adsorption. AIChE Journal. 1965;11:121–125. DOI: 10.1002/aic.690110125

[25] Frenkel D, Smit B. Understanding Molecular Simulation: From Algorithms to Applications. 2nd ed. San Diego: Academic Press; 2002.

[26] Getman RB, Bae YS, Wilmer CE, Snurr RQ. Review and analysis of molecular simulations of methane, hydrogen, and acetylene storage in metal-organic frameworks. Chemical Reviews. 2012;112:703–723. DOI: 10.1021/cr200217c

[27] Lennard-Jones JE. Cohesion. Proceedings of the Physical Society. 1931;43:461–482. DOI: 10.1088/0959-5309/43/5/301

[28] Morse PM. Diatomic molecules according to the wave mechanics. II. Vibrational levels. Physical Review. 1929;34:57–64. DOI: 10.1103/PhysRev.34.57

[29] Rappe AK, Casewit CJ, Colwell KS, Goddard WA, Skiff WM. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. Journal of the American Chemical Society. 1992;114:10024. DOI: 10.1021/ja00051a040

[30] Mayo SL, Olafson BD, Goddard WA. DREIDING: a generic force field for molecular simulations. Journal of Physical Chemistry C. 1990;94:8897–8909. DOI: 10.1021/j100389a010

[31] Bordiga S, Vitillo JG, Ricchiardi G, Regli L, Cocina D, Zecchina A, et al. Interaction of hydrogen with MOF-5. Journal of Physical Chemistry B. 2005;109:18237–18242. DOI: 10.1021/jp052611p

[32] Sagara T, Klassen J, Ganz E. Computational study of hydrogen binding by metal-organic framework-5. Journal of Chemical Physics. 2004;121:12543–12547. DOI: 10.1063/1.1809608

[33] Sagara T, Ortony J, Ganz E. New isoreticular metal-organic framework materials for high hydrogen storage capacity. Journal of Chemical Physics. 2005;123:214707. DOI: 10.1063/1.2133734

[34] Sagara T, Klassen J, Ortony J, Ganz E. Binding energies of hydrogen molecules to isoreticular metal-organic framework materials. Journal of Chemical Physics. 2005;123:014701. DOI: 10.1063/1.1944730

[35] Yang Q, Zhong C. Molecular simulation of adsorption and diffusion of hydrogen in metal-organic frameworks. Journal of Physical Chemistry B. 2005;109:11862–11864. DOI: 10.1021/jp051903n

[36] Yang Q, Zhong C. Understanding hydrogen adsorption in metal-organic frameworks with open metal sites: a computational study. Journal of Physical Chemistry B. 2006;110:655–658. DOI: 10.1021/jp055908w

[37] McDaniel JG, Li S, Tylianakis E, Snurr RQ, Schmidt JR. Evaluation of force field performance for high-throughput screening of gas uptake in metal-organic frameworks. Journal of Physical Chemistry C. 2015;119:3143–3152. DOI: 10.1021/jp511674w

[38] Potoff JJ, Siepmann JI. Vapor-liquid equilibria of mixtures contaning alkanes, carbon dioxide, and nitrogen. AIChE Journal. 2001;47:1676–1682. DOI: 10.1002/aic.690470719

[39] Rankin RB, Liu J, Kulkarni AD, Johnson JK. Adsorption and diffusion of light gases in ZIF-68 and ZIF-70: a simulation study. Journal of Physical Chemistry C. 2009;113:16906–16914. DOI: 10.1021/jp903735m

[40] Manz TA, Sholl DS. Chemically meaningful atomic charges that reproduce the electrostatic potential in periodic and nonperiodic materials. Journal of Chemical Theory and Computation. 2010;6:2455–2468. DOI: 10.1021/ct100125x

[41] Xu Q, Zhong C. A general approcah for estimating framework charges in metal organic frameworks. Journal of Physical Chemistry C. 2010;114:5035–5042. DOI: 10.1021/jp910522h

[42] Wilmer CE, Kim KC, Snurr RQ. An extended charge equilibration method. Journal of Physical Chemistry Letters. 2012;3:2506–2511. DOI: 10.1021/jz3008485

[43] Francl MM, Carey C, Chirlian LE, Gange DM. Charges fit to electrostatic potentials. II. Can atomic charges be unambiguously fit to electrostatic potentials? Journal of Computational Chemistry. 1996;17:367–383. DOI: 10.1002/(SI-CI)1096-987X(199602)17:3<367::AID-JCC11>3.0.CO;2-H

[44] Wilmer CE, Snurr RQ. Towards rapid computational screening of metal-organic frameworks for carbon dioxide capture: calculation of framework charges via charge equilibration. Chemical Engineering Journal. 2011;171:775–781. DOI: 10.1016/j.cej.2010.10.035

[45] Bae Y-S, Snurr RQ. Development and evaluation of porous materials for carbon dioxide separation and capture. Angewandte Chemie International Edition. 2011;50:11586–11596. DOI: 10.1002/anie.201101891

[46] Krishna R, van Baten JM. In silico screening of metal-organic frameworks in separation applications. Physical Chemistry Chemical Physics. 2011;13:10593–10616. DOI: 10.1039/C1CP20282K

[47] Ozturk TN, Keskin S. Predicting gas separation performances of porous coordination networks using atomistic simulations. Industrial & Engineering Chemistry Research. 2013;52:17627–17639. DOI: 10.1021/ie403159c

[48] Keskin S, Sholl DS. Screening metal-organic framework materials for membrane-based methane/carbon dioxide separations. Journal of Physical Chemistry C. 2007;111:14055–14059. DOI: 10.1021/jp075290l

[49] Wiersum AD, Chang JS, Serre C, Llewellyn PL. An adsorbent performance indicator as a first step evaluation of novel sorbents for gas separations: application to metal-organic frameworks. Langmuir. 2013;29:3301–3309. DOI: 10.1021/la3044329

[50] Keskin S. Atomistic simulations for adsorption, diffusion, and separation of gas mixtures in zeolite imidazolate frameworks. Journal of Physical Chemistry C. 2011;115:800–807. DOI: 10.1021/Jp109743e

[51] Atci E, Erucar I, Keskin S. Adsorption and transport of CH_4, CO_2, H_2 mixtures in a bio-MOF material from molecular simulations. The Journal of Physical Chemistry C. 2011;115:6833–6840. DOI: 10.1021/jp200429x

[52] Erucar I, Keskin S. Separation of CO$_2$ mixtures using Zn(bdc)(ted)0.5 membranes and composites: a molecular simulation study. The Journal of Physical Chemistry C. 2011;115:13637–13644. DOI: 10.1021/jp203522u

[53] Erucar I, Keskin S. High CO$_2$ selectivity of an amine-functionalized metal organic framework in adsorption-based and membrane-based gas separations. Industrial & Engineering Chemistry Research. 2013;52:3462–3472. DOI: 10.1021/ie303343m

[54] Keskin S. Gas adsorption and diffusion in a highly CO$_2$ selective metal-organic framework: molecular simulations. Molecular Simulation. 2013;39:14–24. DOI: 10.1080/08927022.2012.700485

[55] Keskin S. High CO$_2$ selectivity of a microporous metal-imidazolate framework: a molecular simulation study. Industrial & Engineering Chemistry Research. 2011;50:8230–8236. DOI: 10.1021/Ie200540y

[56] Babarao R, Jiang JW, Sandler SI. Molecular simulations for adsorptive separation of CO$_2$/CH$_4$ mixture in metal-exposed, catenated, and charged metal-organic frameworks. Langmuir. 2009;25:6590–6590. DOI: 10.1021/la803074g

[57] Bae Y-S, Mulfort KL, Frost H, Ryan P, Punnathanam S, Broadbelt LJ, et al. Separation of CO$_2$ from CH$_4$ using mixed -ligand metal-organic frameworks. Langmuir. 2008;24:8592–8598. DOI: 10.1021/la800555x

[58] Liu B, Smit B. Molecular simulation studies of separation of CO$_2$/N$_2$, CO$_2$/CH$_4$, and CH$_4$/N$_2$ by ZIFs. Journal of Physical Chemistry C. 2010;114:8515–8522. DOI: 10.1021/jp101531m

[59] Chen YF, Nalaparaju A, Eddaoudi M, Jiang JW. CO$_2$ adsorption in mono-, di- and trivalent cation-exchanged metal-organic frameworks: a molecular simulation study. Langmuir. 2012;28:3903–3910. DOI: 10.1021/la205152f

[60] Keskin S, Sholl DS. Assessment of a metal-organic framework membrane for gas separations using atomically detailed calculations: CO$_2$, CH$_4$, N$_2$, H$_2$ mixtures in MOF-5. Industrial & Engineering Chemistry Research. 2009;48:914–922. DOI: 10.1021/ie8010885

[61] Keskin S, Sholl DS. Efficient methods for screening of metal organic framework membranes for gas separations using atomically detailed models. Langmuir. 2009;25:11786–11795. DOI: 10.1021/la901438x

[62] Yang QY, Zhong CL. Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks. Journal of Physical Chemistry B. 2006;110:17776–17783. DOI: 10.1021/Jp062723w

[63] Yang Q, Chunyu X, Zhong C, Chen J-F. Molecular simulation of separation of CO$_2$ from flue gases in Cu-BTC metal-organic framework. AIChE Journal. 2007; 53:2832–2840. DOI: 10.1002/aic.11298

[64] Babarao R, Hu ZQ, Jiang JW, Chempath S, Sandler SI. Storage and separation of CO_2 and CH_4 in silicalite, C-168 schwarzite, and IRMOF-1: a comparative study from Monte Carlo simulation. Langmuir. 2007;23:659–666. DOI: 10.1021/La062289p

[65] Liu B, Smit B. Comparative molecular simulation study of CO_2/N_2 and CH_4/N_2 separation in zeolites and metal-organic frameworks. Langmuir. 2009;25:5918–5926. DOI: 10.1021/la900823d

[66] Han SS, Jung DH, Heo J. Interpenetration of metal organic frameworks for carbon dioxide capture and hydrogen purification: good or bad? Journal of Physical Chemistry C. 2013;117:71–77. DOI: 10.1021/jp308751x

[67] Battisti A, Taioli S, Garberoglio G. Zeolitic imidazolate frameworks for separation of binary mixtures of CO_2, CH_4, N_2 and H_2: a computer simulation investigation. Microporous and Mesoporous Materials. 2011;143:46–53. DOI: 10.1016/j.micromeso.2011.01.029

[68] Atci E, Keskin S. Understanding the potential of zeolite imidazolate framework membranes in gas separations using atomically detailed calculations. Journal of Physical Chemistry C. 2012;116:15525–15537. DOI: 10.1021/Jp305684d

[69] Yilmaz G, Ozcan A, Keskin S. Computational screening of ZIFs for CO_2 separations. Molecular Simulations. 2014;41; 713-726. DOI: 10.1080/08927022.2014.923568

[70] Ozcan A, Keskin S. Effects of molecular simulation parameters on predicting gas separation performance of ZIFs. Journal of Chemical Technology and Biotechnology. 2015;90:1707–1718. DOI: 10.1002/jctb.4482

[71] Ma SQ, Zhou HC. Gas storage in porous metal-organic frameworks for clean energy applications. Chemical Communications. 2010;46:44–53. DOI: 10.1039/B916295j

[72] Ozturk TN, Keskin S. Computational screening of porous coordination networks for adsorption and membrane-based gas separations. Journal of Physical Chemistry C. 2014;118:13988–13997. DOI: 10.1021/Jp5033977

[73] Tong MM, Yang QY, Zhong CL. Computational screening of covalent organic frameworks for CH_4/H_2, CO_2/H_2 and CO_2/CH_4 separations. Microporous and Mesoporous Materials. 2015;210:142–148. DOI: 10.1016/j.micromeso.2015.02.034

[74] Li ZJ, Xiao G, Yang QY, Xiao YL, Zhong CL. Computational exploration of metal-organic frameworks for CO_2/CH_4 separation via temperature swing adsorption. Chemical Engineering Science. 2014;120:59–66. DOI: 10.1016/j.ces.2014.08.003

[75] Haldoupis E, Nair S, Sholl DS. Finding MOFs for highly selective CO_2/N_2 adsorption using materials screening based on efficient assignment of atomic point charges. Journal of the American Chemical Society. 2012;134:4313–4323. DOI: 10.1021/Ja2108239

[76] Watanabe T, Sholl DS. Accelerating applications of metal-organic frameworks for gas adsorption and separation by computational screening of materials. Langmuir. 2012;28:14114–14128. DOI: 10.1021/la301915s

[77] Haldoupis E, Nair S, Sholl DS. Efficient calculation of diffusion limitations in metal organic framework materials: a tool for identifying materials for kinetic separations. Journal of the American Chemical Society. 2010;132:7528–7539. DOI: 10.1021/ja1023699

[78] Lin LC, Berger AH, Martin RL, Kim J, Swisher JA, Jariwala K, et al. In silico screening of carbon-capture materials. Nature Materials. 2012;11:633–641. DOI: 10.1038/NMAT3336

[79] Wilmer CE, Farha OK, Bae YS, Hupp JT, Snurr RQ. Structure-property relationships of porous materials for carbon dioxide separation and capture. Energy & Environmental Science. 2012;5:9849–9856. DOI: 10.1039/c2ee23201d

[80] Krishna R, Long JR. Screening metal-organic frameworks by analysis of transient breakthrough of gas mixtures in a fixed bed adsorber. Journal of Physical Chemistry C. 2011;115:12941–12950. DOI: 10.1021/jp202203c

[81] Krishna R, van Baten JM. A comparison of the CO$_2$ capture characteristics of zeolites and metal-organic frameworks. Separation and Purification Technology. 2012;87:120–126. DOI: 10.1016/j.seppur.2011.11.031

[82] Zhang K, Nalaparaju A, Jiang JW. CO$_2$ capture in rht metal-organic frameworks: multiscale modeling from molecular simulation to breakthrough prediction. Journal of Materials Chemistry A. 2015;3:16327–16336. DOI: 10.1039/c5ta01866h

[83] Colon YJ, Snurr RQ. High-throughput computational screening of metal-organic frameworks. Chemical Society Reviews. 2014;43:5735–5749. DOI: 10.1039/C4cs00070f

[84] Wu D, Yang QY, Zhong CL, Liu DH, Huang HL, Zhang WJ, et al. Revealing the structure-property relationships of metal-organic frameworks for CO$_2$ capture from flue gas. Langmuir. 2012;28:12094–12099. DOI: 10.1021/la302223m

[85] Yang ZL, Peng X, Cao DP. Carbon dioxide capture by pafs and an efficient strategy to fast screen porous materials for gas separation. Journal of Physical Chemistry C. 2013;117:8353–8364. DOI: 10.1021/jp402488r

[86] Qiao Z, Zhang K, Jiang J. In silico screening of 4764 computation-ready, experimental metal-organic frameworks for CO$_2$ separation. Journal of Materials Chemistry A. 2016;4:2105-2114. DOI: 10.1039/C5TA08984K

[87] Lu XQ, Jin DL, Wei SX, Wang ZJ, An CH, Guo WY. Strategies to enhance CO$_2$ capture and separation based on engineering absorbent materials. Journal of Materials Chemistry A. 2015;3:12118–12132. DOI: 10.1039/c4ta06829g

[88] D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. Angewandte Chemie-International Edition. 2010;49:6058–6082. DOI: 10.1002/anie.201000431

[89] Qiao ZW, Zhou J, Lu XH. Designing new amine functionalized metal-organic frameworks for carbon dioxide/methane separation. Fluid Phase Equilibria. 2014;362:342–348. DOI: 10.1016/j.fluid.2013.10.050

[90] Bahamon D, Vega LF. Systematic evaluation of materials for post-combustion CO_2 capture in a temperature swing adsorption process. Chemical Engineering Journal. 2016;284:438–447. DOI: 10.1016/j.cej.2015.08.098

[91] Sun WZ, Lin LC, Peng X, Smit B. Computational screening of porous metal-organic frameworks and zeolites for the removal of SO_2 and NO_x from flue gases. AIChE Journal. 2014;60:2314–2323. DOI: 10.1002/aic.14467

[92] Yu JM, Balbuena PB. How impurities affect CO_2 capture in metal-organic frameworks modified with different functional groups. Acs Sustainable Chemistry & Engineering. 2015;3:117–124. DOI: 10.1021/sc500607y

[93] Babarao R, Jiang YQ, Medhekar NV. Postcombustion CO_2 capture in functionalized porous coordination networks. Journal of Physical Chemistry C. 2013;117:26976–26987. DOI: 10.1021/jp409361j

[94] Huang HL, Zhang WJ, Liu DH, Zhong CL. Understanding the effect of trace amount of water on CO_2 capture in natural gas upgrading in metal-organic frameworks: a molecular simulation study. Industrial & Engineering Chemistry Research. 2012;51:10031–10038. DOI: 10.1021/ie202699r

[95] Nalaparaju A, Khurana M, Farooq S, Karimi IA, Jiang JW. CO_2 capture in cation-exchanged metal-organic frameworks: Holistic modeling from molecular simulation to process optimization. Chemical Engineering Science. 2015;124:70–78. DOI: 10.1016/j.ces.2014.09.054