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Identifying High-Performance Metal—Organic Frameworks for Low-Temperature Oxygen Recovery from Helium by Computational Screening

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stability of the best-performing structures in the presence of moisture as a means to provide a short list of high-performance materials. In addition to identifying specific materials for oxygen-helium separations, this approach could prove useful for selecting adsorbents for other gas separations.

1. INTRODUCTION

Oxygen and helium have important applications in the aerospace industry. Oxygen (O_2) is a standard propellent in rocket engines, while helium (He) is used for prelaunch pressurization of liquid oxygen and liquid hydrogen tanks and also as a cryogenic agent. In remote settings such as lunar missions, the ability to efficiently recover unused propellant for secondary energy uses could significantly improve mission efficiency. Because this propellant will be mixed with He, it would be useful to develop separations methods to purify O_2 from this mixture that are simultaneously energy-efficient and volume-efficient. The composition of the O_2 /He mixtures relevant in this application is dependent on many mission-specific factors, so it would be desirable to develop separations methods that are viable for a range of mixture compositions.

In addition to the specific aerospace applications mentioned above, oxygen is a crucial chemical with uses in medicine, chemical manufacturing, wastewater treatment, fuel cells, and the paper industry.^{1–3} High-purity oxygen (>99%) is essential in applications including medicine,³ semiconductor processing,⁴ ozone generation,⁵ plasma chemistry,⁵ and oxy-fuel combustion.⁶ Helium plays a vital role as a liquid coolant in medical, scientific, and industrial applications based on its extremely low boiling temperature (4.2 K), inert and nonflammable nature, and small atomic size. Natural gas is currently the primary source of helium, but supply concerns have driven interest in improved extraction methods. $^7\,$

The size, weight, and energy constraints associated with interplanetary missions mean that adsorption-based approaches to oxygen/helium separations are more appealing than processes that are used in related large-scale industry settings such as cryogenic distillation. Adsorption is already used in space-based applications such as managing the CO₂ concentration in spacecraft.^{8,9} Metal–organic frameworks (MOFs) have been studied extensively as promising materials for a wide range of gas separation applications. These materials can be tuned to have a specific surface area, pore size, and chemical functionality based on a wide variety of both metal nodes and organic ligands. Although the thousands of MOFs that exist represent an intriguing opportunity to develop effective separations processes, the large number of these materials makes systematic experimental studies impracti-

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cal.^{10,11} Computational screening based on molecular simulations of adsorption has emerged as a useful complement to direct experimental studies.^{12–18} Data from studies of this kind have also been used to generate machine learning models for the prediction of adsorption properties in large libraries of materials.¹⁹

In this paper, we focus on the task of identifying MOFs and operating conditions suitable for the separation of oxygenhelium mixtures at temperatures that are well below terrestrial ambient conditions. Temperature conditions on the lunar surface vary widely and include nighttime temperatures well below 200 K in polar regions and maximum temperatures lower than 200 K close to the poles.²⁵ Motivated by these temperatures, we focused on finding materials that would be effective at temperatures below 200 K. In addition to the space-based application mentioned above, adsorbents for this separation may also be useful in producing helium in other settings. Here, we considered only physisorption of O_2 and not chemisorption. A separate class of materials exists that has strong O₂ binding due to chemisorption; these materials typically require large temperature swings to release bound oxygen.²⁶ We first use detailed molecular simulations to assess mixture adsorption in six representative MOFs as a function of process conditions. This allows us to define screening metrics that are then applied to a collection of 2932 MOFs from the CoRE MOF database,²⁷ a collection of experimentally derived crystal structures. These calculations give insight into the characteristics that lead to good performance for oxygenhelium separations. This screening is used to identify 10 specific MOFs that are predicted to have good performance for oxygen-helium separations. The suitability of these materials for practical implementation is then considered.

2. METHODS

2.1. PSA Process. We focus on a simple pressure swing adsorption (PSA) process²⁸⁻³⁰ for this application, assuming an adsorption pressure of 5 bar and a desorption pressure of 1 bar. These two pressures are representative of conditions that could be used in an optimized process, but other pressure conditions should also be considered in future development of processes in specific applications. One aim of our calculations is to determine the optimum temperature for this simple PSA process for each MOF.

2.2. Adsorbent Evaluation Metrics. Multiple metrics have been proposed to evaluate the performance of adsorbents for gas separations.^{31,32} Although none of these metrics can capture every detail that emerges from detailed process simulations,³³ they can be a useful way to efficiently compare a large number of materials prior to more detailed modeling of promising materials. We have considered the four metrics listed in Table 1, swing capacity,^{31,33,34} adsorption selectiv-ity,^{31,33,34} regenerability,^{33,35,36} and the so-called adsorbent performance indicator (API).³⁷

For the oxygen-helium mixture, the swing capacity is defined as the difference between the gravimetric uptake of oxygen between the adsorption pressure ($P_{\text{total,ads}} = 5$ bar), $N_{O_2}^{\text{ads}}$, and desorption pressure ($P_{\text{total,des}} = 1$ bar), $N_{O_2}^{\text{des}}$, assuming the same bulk phase compositions at both pressures. Focusing on the swing capacity for O2 in this metric is appropriate because of the weakly adsorbing nature of He. The adsorption selectivity is defined separately at the adsorption and desorption pressures using the same bulk compositions. We

Table 1. Definitions of Adsorbent Evaluation Metrics to Assess MOFs

adsorber	nt evaluation metric	metric formula				
$\Delta N_{ m O_2} \ ({ m mol/kg})$	swing capacity	$\Delta N_{\rm O_2} = N_{\rm O_2}^{ads} - N_{\rm O_2}^{des}$				
$S_{\rm ads,O_2/He}{}^{\rm ads}$	adsorption selectivity	$S_{\rm ads,O_2/He}^{\rm ads} = \frac{N_{O_2}^{\rm ads}/N_{\rm He}^{\rm ads}}{y_{O_2}^{}/y_{\rm He}^{}}$				
API	adsorbent performance indicator	$API = \frac{(\alpha_{O_2/He}^{ads} - 1)^{0.5} (\Delta N_{O_2})^2}{ \Delta H_{ads,O_2} ^l}$				
R	regenerability	$R = \Delta N_{\rm O_2} / N_{\rm O_2}^{\rm ads}$				

emphasize that using the same bulk composition at the adsorption and desorption pressures is for convenience in defining these adsorption metrics. In an actual PSA process, these bulk compositions would of course be different; indeed, this is the central aim of a PSA process. Solely choosing either swing capacity or selectivity as an adsorbent evaluation metric is not advisable as a trade-off typically exists between these two metrics (see Figure S1).^{38,39} The adsorbent performance indicator (API) considers the effect of swing capacity, selectivity, and enthalpy of adsorption, reflecting the trade-off relationships between swing capacity and adsorption selectivity. The API is given by³⁷

$$API = \frac{(\alpha_{O_2/He}^{ads} - 1)^A (\Delta N_{O_2})^B}{|\Delta H_{ads,O_2}|^C}$$
(1)

where A = 0.5, B = 2, C = 1, $\alpha_{O_2/He}^{ads}$ is the average of the adsorption selectivity of oxygen over helium at 5 bar and 1 bar, ΔN_{O_2} is the swing capacity, and $\Delta H_{ads,O_2}$ is the average of the heat of adsorption of oxygen at 5 bar and 1 bar. The regenerability, R, is the ratio of the swing capacity and the total adsorbed amount of oxygen at the adsorption pressure. This parameter estimates the fraction of the available adsorption sites that are used in the PSA process.^{35,36}

2.3. Process Conditions. Six MOFs (SIFSIX-2-Cu, UiO-66, ZIF-8, ScBTC, CuBTC, and FeBTC) were used for initial calculations of possible process conditions. We considered pressures (P) ranging from P = 1 to 7 bar and temperatures (T) varying from T = 100 to 200 K for He/O₂ mixture compositions with mole fractions, x, from 0 to 0.8. The specific conditions are summarized in Table 2. This led to a total of 378 operating conditions for each of the six MOFs listed above. Grand Canonical Monte Carlo (GCMC) simulations were performed at each of these conditions.

2.4. Optimum Temperature for PSA. In PSA processes it is critical to estimate the optimum process temperature for any candidate adsorbent. For the six representative MOFs (SIFSIX-2-Cu, UiO-66, ZIF-8, ScBTC, CuBTC, and FeBTC) that were studied comprehensively, the optimum temperature

Table 2. Process Operating Conditions for Detailed GCMC Simulations of SIFSIX-2-Cu, UiO-66, ZIF-8, ScBTC, CuBTC, and FeBTC

Pressure (bar)	1, 2, 3, 4, 5, 6, 7
Temperature (K)	100, 120, 140, 160, 180, 200
Helium concentration in He/O_2 (mole fraction)	0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8



Figure 1. Average of selectivity of oxygen over helium at total pressures of 5 bar and 1 bar for six representative MOFs as a function of temperature (indicated by symbol color), and bulk O_2/He % molar composition (indicated by symbol size).

at specific mixture compositions was identified as the temperature at which each adsorbent shows the maximum API or maximum swing capacity when $P_{\text{total,ads}} = 5$ bar and $P_{\text{total,des}} = 1$ bar.

Our adsorption isotherm for these six MOFs (see Figures S2 and S3) and previous studies on oxygen storage⁴⁰ suggest that single-component O_2 physisorption in MOFs can reasonably be approximated using a Langmuir isotherm. Because the adsorption of He is weak, the resulting Langmuir isotherm is also a reasonable approximation for oxygen adsorption from oxygen/helium mixtures. If a Langmuir isotherm is used then a deterministic approach exists to find the optimum temperature for maximizing swing capacity for single-component adsorption given the adsorption and desorption pressures.⁴¹ This optimum temperature is

$$T_{\rm opt} = \frac{\Delta H^0}{\left[\Delta S^0 + \left(\frac{R}{2}\right) \ln\left(\frac{P_i P_2}{P_0^2}\right)\right]}$$
(2)

where P_1 is the adsorption pressure, P_2 is the desorption pressure, P_0 is the standard pressure (1 bar), ΔH^0 (kJ/mol) is the isosteric heat of adsorption, and ΔS^0 (kJ/mol·K) is the entropy change on adsorption. We show below that ΔS^0 for O_2 adsorption in MOFs is nearly independent of the identity of the MOF using data from the six materials listed above.

Equation 2 was used to estimate the optimum temperature for 2932 MOFs from the CoRE MOF database. For an ideal Langmuir isotherm, ΔH^0 is independent of temperature. In real materials that have binding sites of varying energies, ΔH^0 can vary with temperature.⁴² Figure S4 shows the variation of heat of adsorption of oxygen with temperature in the six materials listed above MOFs. In principle, this information could be combined with eq 2 to refine the prediction of the optimum temperature for PSA. We found, however, that assuming a temperature-independent heat of adsorption works reasonably well in predicting optimum temperatures (see Figure S8 and Table S5). As a result, we predicted the optimum temperatures for 2932 MOFs using eq 2 using the heat of adsorption at 150 K computed using Widom insertion calculation with the RASPA package.⁴³ MOFs with a predicted optimum temperature between 100 and 300 K, 2743 of the initial 2932 materials, were further considered for multicomponent oxygen-helium GCMC simulations to estimate the adsorbent evaluation metrics.

2.5. Molecular Simulation Details. GCMC simulations of oxygen-helium mixture adsorption were carried out in welldefined MOF crystal structures using the RASPA package. Force field parameters for O₂ and helium were taken from the TraPPE⁴⁴ force field. Lennard-Jones (LJ) parameters for the framework atoms were taken from the Universal Force Field (UFF).⁴⁵ Van der Waals interaction between framework atoms and adsorbates was described by combining parameters from the UFF for MOF atoms and from the TraPPE force field for O₂ and helium using the Lorentz-Berthelot mixing rule.⁴⁶ Force fields based on similar principles have been shown to give adsorption energies in good agreement with dispersioncorrected density functional theory (DFT) calculations in a wide variety of MOFs for adsorption of hydrocarbons¹⁵ and CO₂⁴⁷ All Lennard-Jones potentials were truncated at a cutoff of 12.8 Å with analytical tail correction terms. All electrostatic interactions were calculated using the Ewald summation method.⁴⁶ For our initial calculations, a charge-optimized CuBTC MOF structure is taken from CORE MOF database, the SIFSIX-2-Cu structure was obtained from a recent anion pillared MOF database,¹⁶ and FeBTC, ScBTC, UiO-66, and ZIF-8 structures were taken from the CCDC database.⁴⁸ To assign atomic charges to the CCDC MOF structures, each structure was optimized using plane-wave DFT calculations with PBE functional using the VASP code, and subsequently, atomic charges were obtained by the DDEC6 method⁴⁹⁻⁵¹ to be consistent with the other structures listed above. The DDEC partial charges properly reproduce the electrostatic potential in the MOF pores and hence provide an accurate representation of electrostatic interactions between the MOF and the adsorbates with polar and quadrupolar interactions.⁴⁹

All frameworks were considered as rigid during GCMC simulations. Random translation, rotation, reinsertion, and swap moves with equal probability along with identity change were attempted in the simulation cell. Simulations of SIFSIX-2-Cu, CuBTC, FeBTC, ZIF-8 used 5000 initialization and 50000 equilibration cycles while simulations of UiO-66 and ScBTC used 5000 initialization and 20000 equilibration cycles. For all GCMC calculations in computational screening, 5000 initialization cycles and 50,000 production cycles were run. Previous studies have indicated these choices are adequate to get well-converged results.⁴⁰

When screening MOFs we used the 2743 structures mentioned above from the CoRE MOF database that have DDEC charges reported for framework atoms.²⁷ GCMC

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simulations for these materials used the same methods as described above, with pretabulated energy grids with a 0.1 Å spacing to accelerate these simulations. In our screening, we focused on an equimolar oxygen and helium bulk mixture. Only two pressure points, $P_{\text{total,ads}} = 5$ bar and $P_{\text{total,des}} = 1$ bar at the estimated optimum temperature for each MOF were considered since this is sufficient to define the adsorbent evaluation metrics defined above. For each MOF, structural properties such as largest cavity diameter (LCD), pore limiting diameter (PLD), density, void fraction, and surface area were obtained from previous studies of the CoRE MOF database.^{40,52,53}

3. RESULTS AND DISCUSSION

The six MOFs we simulated in detail as listed in Table 2 each showed high selectivity for oxygen over helium (see Figure 1). The selectivity for oxygen in each MOF increases considerably as the temperature is decreased and less strongly as the oxygen content in the bulk mixture increases. The highest selectivity observed in our simulations is for UiO-66 at 100 K, for which a selectivity of 1.62×10^5 was computed for a 20% O₂/He mixture composition.

One way to estimate the optimum temperature for these MOFs is to choose the temperature (100, 120, 140, 160, 180, or 200 K) that gives the maximum API for each bulk oxygenhelium mixture composition (see Table S1). Except for ScBTC, the optimum temperature by this definition for each MOF is independent of the bulk mixture compositions when the bulk concentration of oxygen is below 50%. For more oxygen-rich bulk compositions, the optimum temperature for each MOF is higher. For ScBTC, the optimum temperature found for a 90% mixture composition is 180 K, while at the other mixture compositions we tested it is 120 K. Because the observed optimum temperatures are only weakly dependent on the bulk composition, we focus below on equimolar bulk mixtures. Figure 2 summarizes the results for these mixtures. The API balances the contributions of selectivity and swing capacity, and Figure 2 shows that swing capacity is more decisive in determining which MOF has the highest API.



Figure 2. Adsorbent evaluation metrics for equimolar bulk mixtures at the optimum temperature based on maximizing API for six representative MOFs, with heats of adsorption in kJ/mol. The optimum temperature for each MOF is shown under the MOF's name.

An alternative approach to defining the optimum temperature for a MOF is to maximize the swing capacity for each mixture composition rather than the API. The performance metrics for the same six MOFs at the temperatures defined in this way for equimolar bulk mixtures are shown in Figure S5. Using this alternative definition of the optimum temperature gives a similar dependence of optimum temperature on mixture composition as the definition based on the API (see Table S1), although there is some variation for ScBTC. This is not unexpected since the API includes information from the swing capacity.

Establishing the optimum operating temperature by a careful search of possible temperatures is feasible for detailed simulations of a small number of MOFs but would be inefficient for screening large collections of materials. We noted above that our detailed simulations and previous studies⁴⁰ suggest that in many cases oxygen adsorption in MOFs can be reasonably approximated with a Langmuir adsorption isotherm. With this approximation eq 2 can be used to estimate the optimum temperature for a MOF at specific mixture composition using P_1 (P_2) as the partial pressure of oxygen during adsorption (desorption). Equation 2 defines the optimum temperature for maximizing the swing capacity, and to use this approach the entropy change ΔS^0 must be known. The entropy change implied by equating the optimum temperatures from our detailed simulations with the predictions of eq 2 is shown in Figure 3. There is a small imprecision in these results because our search for the optimum temperature with our simulation data only yielded the optimal temperature with a precision of ± 10 K. These results show that the entropy change does not change significantly with temperature, mixture composition, or the identity of the MOF. This is reasonable because the entropy change is dominated by the reduction in entropy from a free molecule in the gas phase to a highly confined molecule inside a MOF pore. For our screening calculations below we assumed that $\Delta S^0 = -10.22R$ for all temperatures and adsorbents, with this value obtained by averaging the data in Figure 3.

3.1. Computational Screening of CORE MOF Database. Using the insights obtained from the detailed calculations described above, we performed calculations for 2932 MOFs from the CoRE MOF database to find highperforming MOFs for oxygen recovery from helium using a PSA process with an adsorption pressure of 5 bar and a desorption pressure of 1 bar. For each MOF, we first estimated the optimum operating temperature using eq 2 using the heat of adsorption of oxygen computed from a molecular simulation at 150 K and an assumed entropy change on adsorption of ΔS^0 = -10.22*R*. 2743 of these materials were found to have optimal operating temperatures between 100 to 300 K, and these MOFs were considered further.

Once the optimal temperature was estimated for a MOF, GCMC simulations were performed for an equimolar bulk mixture at the adsorption and desorption pressures. This allowed us to calculate the swing capacity, the selectivity of oxygen over helium, and the API for each MOF. Figures 4 and S6 illustrate the correlations between these metrics and the MOF's PLD, LCD, void fraction, and surface area.

Figure 4a shows, as expected, a trade-off between swing capacity and selectivity. Although none of the materials lie in the upper right-hand region of the plot, there are a number of MOFs with high-swing-capacity region with selectivity in the range of 70–200. Figure 4a also shows that high swing capacity



Figure 3. Entropy change ΔS^0 for the adsorption of oxygen in MOF inferred from detailed molecular simulations of six MOFs as defined in the text using eq 2. Data at different temperatures and in different MOFs are indicated by symbol color and symbol type, respectively.



Figure 4. Structure–property relationships for oxygen–helium separation: (a) average selectivity as a function of swing capacity and void fraction, (b) average selectivity as a function of swing capacity and optimum temperature, (c) swing capacity as a function of LCD and heat of adsorption, and (d) swing capacity as a function of gravimetric surface area and void fraction.

Table 5. Top To Structures Identified from Computational Screening Ranked Dased on Swing Car
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rank	CCDC ref code	$\Delta N_{ m O_2}$	$S_{O_2/He}$	API	LCD	PLD	VF	GSA	OMS	$\Delta H_{ m ads,O_2}$	T_{opt}
1	ODIXEG	22.8	83	399	10.36	7.47	0.78	4164	yes	-12	151
2	HAFTOZ	19.9	73	321	15.37	7.52	0.78	3683	no	-11	147
3	XEBHOC	17.7	205	352	12.08	9.91	0.81	4693	yes	-13	126
4	LURGEL	17.0	115	240	6.95	4.98	0.54	1408	no	-13	153
5	XAWVUN	15.6	213	273	10.79	9.22	0.81	4721	yes	-13	125
6	ANUGIA	13.6	201	196	13.85	6.76	0.79	4061	yes	-13	140
7	JEJWOL	13.6	144	168	9.81	7.51	0.75	3472	yes	-13	148
8	BICDAU	13.5	172	179	11.50	6.69	0.78	3655	yes	-13	141
9	HIGRIA	12.4	186	155	11.33	6.86	0.77	3628	yes	-14	139
10	NEDWIE	12.2	130	129	8.99	6.43	0.72	3133	yes	-13	151

 ${}^{a}\Delta N_{O_2}$ is the swing capacity (mol/kg), $S_{O_2/He}$ is the average selectivity of oxygen over helium at total pressures of 5 bar and 1 bar, API is the adsorbent performance indicator, LCD is the largest cavity diameter (Å), PLD is the pore limiting diameter (Å), VF is the void fraction, GSA is the gravimetric surface area (m²/g), OMS indicates the presence of open metal sites, $\Delta H_{ads,O_2}$ is the average of heat of adsorption of oxygen (kJ/mol) at total pressures of 5 bar and 1 bar at optimum temperature, and T_{opt} is the optimum temperature (K) for PSA.



Figure 5. Variation of oxygen swing capacity with temperature in the vicinity of the predicted optimum temperature for the materials listed in Table 3.

is associated with MOFs with large void fractions, similar to previous studies of CO_2 adsorption.¹³ In Figure 4b, we can see that MOFs with swing capacity greater than 12 mol/kg have optimum operating temperatures from 125 to 155 K. In general, MOFs with higher void fractions are seen to have lower optimum temperatures. Figure 4c shows that MOFs with high swing capacity typically have a heat of adsorption for oxygen from -11 to -14 kJ/mol. In Figure 4d, some of the MOFs with high swing capacity have gravimetric surface areas between 3500 and 4500 m²/g.

Table 3 lists the top 10 MOFs from the 2743 MOFs we considered based on swing capacity, along with selected structural properties of these MOFs. These 10 materials have swing capacities for oxygen of 12–23 mol/kg, compared to values of 4–15 mol/kg for the six MOFs we considered in detail in Figure 2. Table S2 lists the top 10 structures if the ranking of materials is based on the API. Both these rankings have a total of 9 structures in common. There is not a strong correlation between swing capacity and gravimetric surface area for the overall set of materials (Figure 4d), but the top 3 MOFs have surface areas exceeding 3600 m²/g. 9 of the 10 structures in Table 3 have void fractions exceeding 0.7. Many of the materials in the CoRE MOF database have open metal sites (OMS) and 8 of the 10 structures in Table 3 possess open metal sites (OMS).

Equation 2 only provides an estimate of the optimum temperature for PSA for a given material. We therefore used GCMC simulations to obtain the swing capacity for each material in Table 3 for a range of temperatures in the vicinity of estimated optimum temperature (see Figure 5). These results showed that the uncertainty in the optimum temperature predicted by eq 2 was 10-20 K. This uncertainty arises from the approximations used in eq 2, including the assumption that oxygen adsorption follows a Langmuir adsorption is otherm and that the entropy change on adsorption is equal for all materials.

Our approach has identified a set of MOF candidates among several thousand structures with highly favorable properties for oxygen/helium separations, including materials that have a swing capacity larger than 20 mol/kg. Figure S7 shows the oxygen adsorption isotherms for these top 10 MOFs, and Table S4 lists the observed optimum temperatures, swing capacity, and API for each material as determined from the GCMC results shown in Figure 5. Figure 5 illustrates another aspect of material selection that may be important for practical applications, namely, then it may be worth using materials with a slightly lower swing capacity (e.g., LURGEL, JEJWOL, BICDAU, HIGRIA) where the variation in this swing capacity with operating temperature is less pronounced than other choices (e.g., ODIXEG, HAFTOZ, XEBHOC, XAWVUN). We have not considered temperature swing adsorption (TSA) in this work, but materials in which the swing capacity is strongly temperature-dependent (e.g., XEBHOC, XAWVUN) may be interesting initial candidates to consider as a TSA-based separation was desirable.

3.2. Water Stability and Previous Syntheses of Best-Performing MOFs. The stability of MOFs with respect to exposure to water is an important issue in various applications.⁵⁴ Unfortunately, many MOFs are unstable in water. The water stability of a MOF is also a useful proxy for how readily a MOF could be deployed in a practical application, even if that final application would not involve the presence of moisture, since MOFs that are unstable to water exposure are likely to require specialized handling during synthesis, formulation, and storage. A challenge with assessing the water stability of large collections of MOFs is that experimental data is only available for a small fraction of known materials. To address this challenge, Batra et al. developed a Machine Learning (ML) model to predict the water stability of MOFs using chemical features capturing information about their constituent metal nodes, organic ligands, and metal-ligand molar ratios. This ML model classifies MOFs into two categories, namely, unstable/low kinetic stability and high kinetic stability/stable.⁵⁵ MOFs that are classified as unstable are expected to show little structural stability after exposure to even small amounts of moisture in the vapor phase.⁵⁶ We used the ML model of Batra et al. to predict the water stability of the top 25 MOFs identified from the computational screening above. Table S6 shows the resulting water stability predictions. More than half of these potential MOF candidates are predicted to have poor stability in the presence of water, which likely means that they are poorly suited to practical applications.

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By combining our computational screening and predictions of water stability, we recommend the MOFs HAFTOZ, LURGEL, JEJWOL, BICDAU, and HIGRIA as viable candidates for more detailed consideration as adsorbents for low-temperature oxygen/helium separations. Each of these materials has strong selectivity for oxygen over helium, high swing capacity for oxygen adsorption, and is predicted to be stable to water exposure. The oxygen swing capacity, average selectivity, and optimum operating temperature (as determined from the GCMC calculations used in Figure 5) for PSA between pressures of 5 bar and 1 bar for these MOFs are summarized in Table S7.

A factor that is often neglected in large-scale computational screening of MOFs as adsorbents is the ease with which the candidate MOF can be synthesized and scaled up. We partially addressed this issue by focusing attention on materials that are expected to be stable to water exposure. Another partial piece of information about ease of synthesis can be gained from the number of separate experiments for a MOF that have been previously reported. A systematic study of this issue by Agrawal et al. concluded that a very large majority of all reported MOFs have only been studied experimentally in a single paper, while a handful of so-called "super-MOFs" have been synthesized in hundreds of separate experimental reports.⁵⁷ For each of the five MOFs in Table S7, we examined all published papers that cite the original experimental report, giving the results summarized in Table S8. Following the analysis of Agrawal et al., we distinguished between an exact resynthesis, which produced the same material as the original report, and modified synthesis, which reported a derivative of the original materials (for example, with a different linker or metal center). We found no reports with an exact resynthesis of HAFTOZ or JEJWOL, and LURGEL has been resynthesized only once by same authors as the original report. This situation is consistent with the conclusions of Agrawal et al. that the synthesis of many MOFs has only been reported once in published reports. BICDAU and HIGRIA, however, have been resynthesized multiple times by multiple groups. This observation suggests that BICDAU and HIGRIA are likely to be promising initial choices for experimental testing among the candidates we have identified for oxygen and helium separation application.

4. SUMMARY AND CONCLUSIONS

Separation of oxygen/helium mixtures at low temperatures using pressure swing adsorption may be useful in space-based settings where recovery of unused propellant may be desirable. We used a computational screening approach to identify highperformance MOFs for this application and their corresponding PSA operating temperatures to maximize the swing capacity for oxygen. Our approach allowed us to consider a collection of several thousand MOFs with experimentally derived crystal structures. Selecting an adsorbent for a practical separation must consider multiple performance characteristics, and a trade-off between various characteristics often dictates the appropriate choice among multiple materials. For example, we have emphasized gravimetric adsorption capacity in our screening because of the critical importance of mass in spacebased applications, but it also desirable for an adsorbent to have a high volumetric adsorption capacity. If the five materials in Table S7 are ranked by volumetric swing capacity, the top three materials are HAFTOZ, BICDAU, and HIGRIA. These three MOFs have similar void fraction and surface area however different material densities. MOF with low density

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and show higher volumetric swing capacity. Another example of a trade-off that may have practical implications was discussed in the context of Figure 5 in terms of selecting materials whose performance for PSA is not strongly temperature-dependent.

For the top 25 structures with favorable adsorption properties identified from screening we predicted the water stability of each material, using this stability as a proxy for the ease of working with the materials in practical settings. This led to a set of five recommended MOFs that are expected to be stable to water exposure and which have swing capacities for oxygen of 14-21 mol/kg for PSA based on a pressure range of 1-5 bar and equimolar oxygen/helium bulk mixtures. All of these materials have selectivities for oxygen over helium larger than 80. Analysis of the literature that cites the synthesis of the five recommended MOFs showed that only two of these five MOFs have been resynthesized multiple times since their first reported synthesis. These two materials appear to be promising candidates for future experimental studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c03544.

Additional data and computational results (PDF)

Complete collection of data from detailed computational study on six representative MOFs (XLSX); swing capacity, selectivity, and heat of adsorption data obtained from detailed GCMC simulations at various operating conditions; entropy change estimation for these six MOFs, CIF files for the six representative MOFs, namely, SIFSIX-2-Cu, CuBTC, ScBTC, ZIF-8, FeBTC, and UiO-66; complete collection of data from computational screening of 2743 MOFs in a simplified form (XLSX); structural properties, predicted optimum temperatures, swing capacity, selectivity, and API for 2743 MOFs; and isotherm data and temperature sensitivity analysis data for identified top 10 MOFs (ZIP)

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Notes

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