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PAPER

Structure–property relationships of porous materials for carbon dioxide separation and capture[†]

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There is an urgent need to identify porous materials that can efficiently separate CO_2 from mixtures of gases, such as the exhaust of fossil-fuel-based power plants and from impure sources of CH_4 (*e.g.*, natural gas and landfill gas). Recently, researchers have investigated collections of porous metal–organic frameworks (MOFs) with the intent of finding correlations between CO_2 separation ability and various material properties. However, due to the limited size of the collections, no clear correlations were found for material properties such as pore size, surface area, and pore volume, leaving researchers with little guidance in the design of new materials. In this work we drastically expand the scope of previous studies to include over 130 000 hypothetical MOFs, using molecular simulation to generate the adsorption properties. The resulting data exhibit sharply defined structure–property relationships that were not apparent when smaller collections of MOFs were considered. We show clear correlations between purely structural characteristics (*e.g.*, pore size, surface area, and pore volume), as well as chemical characteristics (*i.e.*, functional groups), with five adsorbent evaluation criteria taken from the engineering literature. These reported structure–property relationships can serve as a map for experimental synthesis going forward.

1. Introduction

Due to both rising global greenhouse gas emissions¹ and an increased worldwide demand for natural gas,² there is tremen-

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dous interest in the development of porous materials to separate carbon dioxide (CO₂) from mixtures of gases, such as the exhaust of fossil-fuel-based power plants (flue gas) and gases that are rich sources of methane (CH₄). Flue gas—which is primarily nitrogen (N₂, >70%) and CO₂ (10–15%)—accounts for roughly 33–40% of global CO₂ emissions.³ Capturing CO₂ economically, which would significantly mitigate greenhouse gas emissions, therefore requires a material that can efficiently separate CO₂ from N₂.

Greenhouse gas emissions can also be mitigated by switching to CH₄-based energy sources, which emit comparatively less CO_2 per unit of energy than coal- or petroleum-based fuels. Today, CH₄ is primarily obtained from natural gas, which is typically 80–95% CH₄ and 5–10% CO₂ with small amounts of N₂ and

Broader context

Materials that are "nanoporous" (*i.e.*, that have pore diameters smaller than 10 nanometers) are able to selectively attract or "capture" specific molecular species into their pores at the exclusion of others. Nanoporous materials are, therefore, potentially useful for separating mixtures of gases. However, given a particular gas mixture (*e.g.*, CO_2 and N_2 from the exhaust of fossil-fuelbased power plants), it is a challenge to create a specific nanoporous material that *effectively* separates those particular gases (*e.g.*, captures CO_2 but not N_2). Meeting such a challenge requires that: (1) we are able to *synthesize* the desired geometry and chemical nature of the pores, and that (2) we *know* what the optimal shape, size, and chemistry of the pores ought to be for a given application. Metal–organic frameworks (MOFs) are a ubiquitous class of nanoporous materials that can be customized to have pores of practically any shape, size, and chemical functionality. Thus, MOFs arguably meet the first challenge criterion. However, it is still unknown which of the infinite variety of possible MOFs would be best for certain applications. This work uses large-scale computational simulations to shed light on what kinds of pore are optimal for CO_2 separation and capture.

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heavier hydrocarbons.² A potentially significant source of CH₄ is municipal or industrial landfill gas, which is approximately 40– 60% CO₂. Purifying natural gas and landfill gas by removing CO₂ is essential, both to increase the energy density and because pipelines and fuel tanks used to transport CH₄ become corroded in the presence of acid CO₂ gas.^{4,5}

Porous materials can be used to separate CO_2 from these mixtures *via* pressure-swing adsorption (PSA) or vacuum-swing adsorption (VSA), where the material is exposed to impure gas at a high(er) pressure and then regenerated by lowering (*i.e.*, releasing or "swinging") the pressure. Qualitatively, the effectiveness of a particular porous material depends on how well it adsorbs CO_2 at the higher pressure and then how easily it releases the CO_2 at the lower pressure. In lieu of testing an expensive fullscale PSA process to measure this effectiveness, simple but approximate quantitative performance metrics can instead be calculated from adsorption measurements of pure gases (*i.e.*, as opposed to mixtures). For example, Bae and Snurr recently assessed over forty porous materials based on five "adsorption evaluation criteria" using pure CO_2 , CH_4 , and N_2 adsorption measurements taken from the literature. See Table 1.⁶

Each porous material was scored on these criteria in four distinct cases corresponding to separating CO_2 from either N_2 or CH_4 at pressures and compositions selected for their industrial relevance, namely: (1) natural gas purification using PSA, (2) landfill gas separation using PSA, (3) landfill gas separation using VSA, and (4) flue gas separation using VSA. See Table 2 for gas phase mixture compositions and pressures that approximate each of these four cases (at temperatures of 298 K). Using the evaluation criteria, Bae and Snurr were able to quickly identify promising material candidates for further investigation.

In addition to identifying promising materials for CO_2 separations, for certain cases Bae and Snurr were able to identify correlations between the adsorbent evaluation criteria scores and

Table 1 Evaluation criteria used by Bae and Snurr to assess the effectiveness of porous materials for CO₂ separation and capture.⁶ Here, N is the adsorbed amount and y is the mole fraction in the gas phase. The subscripts 1 and 2 indicate CO₂ and either CH₄ or N₂, respectively. The superscripts "ads" and "des" refer to adsorption and desorption conditions, respectively

Adsorbent evaluation criteria							
CO ₂ uptake under adsorption conditions (mol kg ⁻¹) Working CO ₂ capacity (mol kg ⁻¹), $N_1^{ads} - N_1^{des}$ Regenerability (%), $(\Delta N_1/N_1^{ads}) \times 100\%$ Selectivity under adsorption conditions, $(N_1^{ads}/N_2^{ads})(y_2/y_1)$ Sorbent selection parameter, $(\alpha_{12}^{ads})^2/(\alpha_{12}^{des})(\Delta N_1/\Delta N_2)$	$N_1^{ m ads} \ \Delta N_1 \ R \ lpha_{12}^{ m ads} \ S$						

the heat of adsorption (Q_{st}) in the materials. Such correlations are useful for simplifying the screening of candidate materials and for providing direction for experimental synthesis. However, it is difficult to design new materials that have an *a priori* chosen Q_{st} value. It is easier to design materials based on a chosen pore size or surface area, or based on a particular chemical functionality. Yet, data reported to date have been too scarce to identify significant correlations between CO₂ separation ability and purely structural (*e.g.*, pore diameter, surface area, and pore volume) or chemical characteristics. Although anecdotal design rules for CO₂ separation have been suggested in the literature,^{7,8} there is a clear need for structure–property relationships emanating from large-scale analysis.

In this work, we expand the scope of Bae and Snurr's survey to include over 130 000 hypothetical metal–organic frameworks (MOFs) that were generated using a recently described algorithm by Wilmer *et al.*⁹ For each MOF, we used established molecular simulation techniques^{10–12} (for details see the ESI†) to obtain the pure component CO₂, CH₄, and N₂ adsorption data required to calculate the five adsorbent evaluation criteria (as shown in Table 1) for the four CO₂ separation cases (as shown in Table 2).

Our work complements several recently reported large-scale computational screening efforts focused on CO₂ separations.^{8,13-16} Lin et al. screened hundreds of thousands of hypothetical zeolite and zeolitic imidazolate framework structures for their application to CO₂ capture from flue gas (which we refer to as "Case 4" in this work), but correlations of performance with structural features were not described.¹⁴ Similarly, Haldoupis et al.8 computationally screened ~500 MOFs for their ability to separate CO₂ from N₂, which was the largest set of predictions for CO₂ adsorption in MOFs at the time it was reported. In their work, Henry's constants were correlated with pore diameters, but similar comparisons with other structural characteristics (e.g., surface area, void fraction) or other adsorption properties (e.g., working capacity, selectivity) were not reported. Recently Wu et al.16 examined 105 MOFs for CO₂/N₂ separations and discovered that simultaneously increasing $Q_{\rm st}$ values while decreasing the void fraction was a useful design rule for increasing the selectivity.

2. Results

With this significantly larger dataset, we were able to observe sharply defined correlations between the five adsorbent evaluation criteria and material properties, such as the pore diameter, surface area, pore volume, and chemical functionality. See Fig. 1 for some representative examples. In general, we observed what could be described as structure–property *domains* whose

Table 2 Evaluation criteria used by Bae and Snurr to assess the effectiveness of porous materials for CO_2 separation and capture.⁶ The four mixture compositions and adsorption/desorption conditions considered are for: (1) natural gas purification using PSA, (2) landfill gas separation using PSA, (3) landfill gas separation using VSA, and (4) flue gas separation using VSA. Temperature is 298 K in all cases

Case	Application	Mixture composition	Adsorption and desorption pressures $(p^{ads} \text{ and } p^{des})$
1	Natural gas purification using PSA	$\begin{array}{l} {\rm CO_2-CH_4=10:90}\\ {\rm CO_2-CH_4=50:50}\\ {\rm CO_2-CH_4=50:50}\\ {\rm CO_2-CH_4=50:50}\\ {\rm CO_2-N_2=10:90} \end{array}$	$p^{ads} = 5$ bar, $p^{des} = 1$ bar
2	Landfill gas separation using PSA		$p^{ads} = 5$ bar, $p^{des} = 1$ bar
3	Landfill gas separation using VSA		$p^{ads} = 1$ bar, $p^{des} = 0.1$ bar
4	Flue gas separation using VSA		$p^{ads} = 1$ bar, $p^{des} = 0.1$ bar



Fig. 1 A sample of structure–property relationships derived from simulated CO₂, CH₄, and N₂ adsorption in over 130 000 hypothetical MOFs. Clear relationships can be discerned between (a) CO₂ working capacity (ΔN_1) and surface area, (b) CO₂ uptake (N_1) at 2.5 bar and CO₂ heat of adsorption (Q_{st}), and (c) selectivity of CO₂ over N₂ (α_{1}^{ads}) and maximum pore diameter. Q_{st} values are determined from CO₂ adsorption at the lowest simulated pressure: 0.01 bar. Each plot is divided into 50 × 50 regions that are represented by a filled circle if more than 25 structures exist within the region. The color of each circle represents the average (d) helium void fraction of all structures in that plot region.

boundaries arise from either the limited diversity of the porous structures in our database or from fundamental physical constraints (as imposed by our simulation model). Here, we make the *assumption* that, when interpreting the simulation data, the boundaries on these domains stem from fundamental physical constraints (see Discussion section for details).

The clear relationships identified in our analysis can help guide future experimental synthesis efforts and focus attention on structural characteristics that are likely to result in materials with desired CO₂ separation abilities (*e.g.*, pore diameters less than \sim 12 Å for flue gas separation applications. See Fig. 1c).

In a large-scale computational analysis, there are a substantial number of possible cross-correlations between various quantifiable material properties and performance. Here, we focus primarily on two material properties, namely, the heat of adsorption of CO₂ and the gravimetric surface area, both of which have received significant attention in the MOF literature. We also address secondarily pore volume and pore diameter, which we have observed to strongly influence CO₂ separation ability. We show correlations found between each characteristic and the five evaluation criteria in each of the four CO2 separation cases. Correlations involving other structural characteristics, such as the volumetric surface area (an example is shown in Fig. 1a), are included comprehensively in the ESI.[†] We also report the frequency of finding specific chemical functional groups in the MOFs as a function of CO₂ separation ability. For example, we found that fluorinated groups are promising in every CO2 separation scenario considered. (See below.) Finally, we identify the combinations of material properties that are shared by the MOFs with the highest CO₂ separation ability (as determined by their sorbent selection parameter value, S, described in Table 1).

2.1 Correlations with the heat of adsorption of CO₂

Our large-scale analysis shows that working capacity drops off steeply whenever Q_{st} is too large or too small, as shown in Fig. 2a. However, while a suboptimal Q_{st} value can preclude a porous material from having a high-working capacity, it is not true that an optimal Q_{st} value is sufficient for good performance. In fact, this is generally observed for all of the evaluation criteria considered: only one structure characteristic has to be wrong for a material to perform poorly, but many characteristics must be optimal for a material to perform well. For example, working capacity in landfill gas separation *via* a PSA process (Fig. 2a, Case 2) is highest at Q_{st} values of ~21 kJ mol⁻¹, but MOFs with the same Q_{st} values are also found to have working capacities close to zero. From Fig. 2a, Case 2, one could surmise that a starting point for designing high-working-capacity materials would be ones with Q_{st} values of ~21 and void fractions of ~0.8. An even better starting point could be achieved by combining these Q_{st} and void fraction characteristics with others described in this article.

Fig. 2b shows that regenerability generally decreases with increasing $Q_{\rm st}$ for all four cases, as has been noted previously.⁶ However, the selectivity (Fig. 2c) and the sorbent selection parameter (S) (Fig. 2d) reach their maxima at optimal Q_{st} values just as the working capacity does. The observation that these parameters rise and fall as functions of Q_{st} , in a manner that is not simply linear, provides a more complete picture beyond Bae and Snurr's observations that selectivity is positively (and linearly) correlated with $Q_{\rm st}$ for all cases except Case 2 and that S values are positively correlated with Q_{st} for Cases 3 and 4 (although a few data points at very high $Q_{\rm st}$ values had notably low S values).⁶ More generally, our data suggest that when one is seeking structure-property insights, fitting one-dimensional functions, whether lines or higher polynomials, may not be as easy or useful as higher dimensional functions. An exception to this trend is possible, as with the regenerability in Fig. 2b, where choosing a suitable constraint (e.g., a fixed void fraction of ~ 0.35) results in a domain that is narrow enough that it can be well-defined by a one-dimensional curve (one can trace a curve by connecting the yellow circles in Cases 1, 3, and 4 in Fig. 2b, but this is not always possible in general).

From Fig. 2, one can readily observe that each case has an optimal void fraction and that higher partial pressures of CO_2 favor greater void fractions. For example, in landfill gas separations using PSA (Case 2), where the partial pressure of CO_2 in



Fig. 2 The relationships between (a) working capacity (ΔN_1), (b) regenerability (R), (c) selectivity (α_{12}^{ads}) and (d) sorbent selection parameter (S) and the heat of adsorption (Q_{st}) of CO₂ for each of the four cases. Each plot is divided into 30 × 30 regions that are represented by a filled circle if more than 10 (or 25 for α_{12}^{ads} and S values due to higher statistical error that results from being an aggregate of the other parameters) structures exist within the region.

the gas phase is 2.5 bar, void fractions of ~0.6 to 0.8 are optimal for α_{12}^{ads} and S values. However, for capturing CO₂ from flue gas using VSA (Case 4), where the partial pressure of CO₂ is 0.1 bar, the optimal α_{12}^{ads} and S values are found at void fractions in the ~0.3 to 0.4 range. This optimal range, taken together with a Q_{st} of ~33 kJ mol⁻¹, results in MOFs with remarkably high S values (>400) for Case 4. Interestingly, Bae and Snurr reported that the ZIF-78 structure,⁷ based on experimental measurements, has an S value of 396 and a Q_{st} of 30 kJ mol⁻¹, which agrees with our observations.

The optimal Q_{st} is highest for Case 4 and lowest for Case 2, suggesting that optimal Q_{st} may be inversely correlated with CO₂ partial pressure, just as is observed for the void fraction. It is worth nothing that only Case 2 benefits from MOFs with very spacious pores (*i.e.*, high void fractions), while the other three cases require only modest void fractions (~0.3 to 0.6) for optimal *S* values (see Fig. 2d). Hence, the race to make MOFs with ever larger pores, though potentially useful for other applications such as gas storage, may be ill-suited for developing optimal CO_2 capture materials (unless very high pressure conditions are considered).

2.2 Correlations with the gravimetric surface area

The surface area is one of the defining structural characteristics of MOFs, but its relationship to CO_2 separation ability (*e.g.*, selectivity, working capacity) has remained unclear. In reports where the number of porous materials was less than fifty, no correlations between surface area and CO_2 separation were observed.^{67,10}

However, we observe several clear trends relating surface area to the five adsorbent evaluation criteria, as shown in Fig. 3. Fig. 3a shows that, amongst the best MOFs with regards to working capacity, ΔN_1 decreases almost linearly with surface area for Cases 1, 3, and 4 after passing through a maximum value in the 1000–2000 m² g⁻¹ range. For Case 2, the highest ΔN_1



Fig. 3 The relationships between the (a) working capacity (ΔN_1), (b) regenerability (R), (c) selectivity (α_{12}^{ads}), and (d) the sorbent selection parameter (S) and the surface area for each of the four cases. Each plot is divided into 30×30 regions that are represented by a filled circle if more than 10 (or 25 for α_{12}^{ads} and S values) structures exist within the region. Although surface areas that are smaller than 200 m² g⁻¹ seem to show good CO₂ separation performances in terms of α_{12}^{ads} and S values, they have low working capacities as shown in (a).

values occur at greater surface areas (~4000 m² g⁻¹) and with larger pore diameters (~8 to 12 Å). Fig. 3b shows that, in contrast to the trend with $Q_{\rm st}$, the regenerability generally *increases* with surface area for all four cases.

Regarding selectivity, we found that pores that are no larger than ~5 to 6 Å have the highest CO_2 selectivity values for Case 4 (see Fig. 1c and 3c). The optimal pore diameters for Cases 1 and 3 are only modestly larger, but the best materials for Case 2 had pores as large as 8–10 Å (see also Fig. S3.3 in the ESI†). Our findings suggest that higher partial pressures of CO_2 (2.5 bar for Case 2) lead to optimal selectivities at larger pore diameters. Conversely, when the partial pressure of CO_2 is low (0.1–0.5 bar for Cases 1, 3, and 4), materials with small pores and high CO_2 heats of adsorption are optimally selective.

Finally, we observed that for optimal S values, only modest surface areas (~ 1000 to 2500 m² g⁻¹) are needed in three of the four Cases (Cases 1, 3, and 4 in Fig. 3d). In each case, the highest

S values, as well as the highest ΔN_1 , and α_{12}^{ads} values, decrease sharply beyond a certain optimal surface area. For Cases 1 and 4, this decrease begins after only ~1000 m² g⁻¹ (see Fig. 3d), which is quite modest in the field of MOFs.¹⁷ This is an important consideration for designing future porous materials, since greater surface area is sometimes viewed as a universally positive trait for porous materials.

Given the large ranges of ΔN_1 , *R*, and α_{12}^{ads} values that are possible for any given surface area and pore diameter combination, it is understandable that it would not have been possible to observe the relationships described above without a sufficiently large and diverse dataset. A subset of materials chosen at random within the structure-property "domains" in Fig. 3 would not reveal any simple relationships. However, the limiting (*i.e.*, highest and lowest) or *bounding* ΔN_1 , *R*, and α_1^{ads} values appear to follow well-defined, if not necessarily well-understood, curves as a function of pore diameter and surface area.

2.3 Correlations with chemical functional groups

There is significant interest in finding the best functional groups for CO_2 capture and recent theoretical¹⁸ and experimental^{7,19,20} reports have studied small sets of MOFs that varied in chemical functionality. However, some have found that variability in pore size and shape dominates CO_2 adsorption effects and thus precludes generalizations about whether certain functional groups are optimal.²⁰

We found that certain chemical functional groups, particularly those with fluorine and chlorine atoms, were frequently among the best performers in all four cases as shown in Fig. 4. Of the MOFs with functional groups depicted in Fig. 4, nearly 50% of those with the highest S values had fluorine groups. This supports the findings of reports that show fluorinated polymer membranes generally have high selectivity for CO₂ over N₂ or CH₄.²¹⁻²³ This is likely due to the polar nature of the fluorine groups, and others have found polarity to be important for CO₂ separation applications.^{6,18} Amine functional groups performed better than alkyl groups, but not as dramatically as one might expect from recent reports in the literature.^{24,25} This may be due to the predominance in our database of amine functional groups that are on aromatic rings rather than amines that terminate an alkyl chain, such as methylamine or ethylamine, in which case the partial charge (predicted by our charge equilibration method¹²) on the nitrogen atom is not as strong. Alternatively, our simple Lennard-Jones + Coulomb force field may not be able to capture the strong CO₂-amine binding observed by others.

2.4 Choosing porous materials for specific cases

Generally we found that one cannot simultaneously optimize a single porous material for all four cases. We looked for



Fig. 4 The relationships between the sorbent selection parameter (*S*) and the occurrence of specific chemical functional groups in the MOFs considered. Among MOFs with the highest *S* values, chlorine (Cl), and fluorine (F) functional groups occur very frequently (>60 to 70% combined) relative to hydrogen (unfunctionalized, H), amine (A), methyl (M), ethyl (E), and propyl (P) groups.

correlations among performance in different cases, using the same adsorbent evaluation criteria (*e.g.*, selectivity for CO_2 in natural gas purification against selectivity for CO_2 in landfill gas separations). We found that when considering the sorbent selection parameter, *S*, performance in Case 1 was inversely correlated with performance in Case 2 as shown in Fig. 5a. In contrast, as shown in Fig. 5b, many MOFs have high *S* values for both Case 1 and Case 4 and almost none of those have high *S* values for Case 2. This suggests that it may be possible to choose optimal MOFs for certain CO_2 partial pressure ranges (in Case 1 and Case 4, the partial pressure of CO_2 is 0.5 bar and 0.1 bar, respectively), but outside of those ranges markedly different structures would be required.



Fig. 5 Correlating the sorbent selection parameters (*S*) for all four cases against each other. The *S* values for Case 1 and Case 2 are inversely correlated, but (a) neither preclude high performance for Case 3, whereas (b) Case 1 is strongly, positively correlated with high performance in Case 4. Each plot is divided into 50×50 regions that are represented by a filled circle if more than 10 structures exist within the region. The color of each circle represents the average *S* value of all structures in that plot region for the corresponding case.





Fig. 6 The material properties of the porous materials that have the highest sorbent selection parameters (S) for specific cases. These MOFs are the top 7.5% (~10 000) in the database of ~137 000 for each case, according to their S value. Each plot is divided into 30×30 regions that are represented by a filled circle if more than 10 structures exist within the region.

One might ask, what are the properties that the best porous materials have in common for a given application? In Fig. 6, we show a selection of property combinations, namely the $Q_{\rm st}$ value, gravimetric surface area, and void fraction, which are shared by the top 7.5% (~10 000) porous materials (according to their S value). In each case, there is a narrow window of $Q_{\rm st}$ values but a relatively broad range of surface area and void fraction combinations. This suggests that some design flexibility is left to optimize for cost, stability, and other characteristics.

3. Discussion

A strength of our approach is that every material is considered in a consistent way, and the sheer number and diversity of materials examined leads to a continuous spectrum of structural characteristics and adsorbent properties. All of our results, however, are derived from a model, which by design, is approximate and suited for high-throughput, large-scale analysis. Therefore, the structure–property relationships are likely distorted to some degree by a systematic error stemming from the approximate nature of our model.

Certain aspects of our model are more likely to contribute to inaccuracy than others. For example, it is known that we are under-predicting the interaction strength of CO₂ with open metal sites¹⁰ that are present in our hypothetical MOF database.⁹ Additionally, as we have shown in past work,¹¹ low loadings of CO₂ can be sensitive to the model of the electrostatic environment inside the pores of the MOF. Here, we have calculated partial atomic charges for all 137 000+ MOFs using our recently described EQeq approach (see ESI† for details). This approach requires an estimate of the dielectric constant, which was conservatively chosen to be 2.0 for all MOFs. This estimate likely led to smaller partial charges than what would have been predicted by higher accuracy DFT based methods,^{26,27} and consequently led to an under-prediction of the electrostatic energy

within the MOFs. The combination of underestimating the interaction strength of open metal sites and under-predicting partial charge magnitudes implies that we have likely underestimated CO_2 adsorption across the board.

It should be noted that we have simulated adsorption at 298 K in each case to facilitate straight-forward comparison with experimental data reported in the literature. However, flue gas (Case 4) at the point of emission is typically closer to 310 K, for which optimal materials might require slightly higher $Q_{\rm st}$ values than reported here.

We must also be cautious in interpreting the significance of the highest and lowest (*i.e.*, bounding) adsorption evaluation criteria values (as depicted in Fig. 2 and 3). These apparent performance limits are no doubt affected by the approximations used in the model and by the fact that we have explored only a portion of the possible porous materials space. Plausible materials exist that are not in our database but that might have higher (or lower) values for the adsorbent evaluation criteria when simulated using the same model. In this work we have assumed, when interpreting the data, that this latter source of error is not significant. However, lacking a rigorous proof that our database is *sufficiently diverse*, the claim that the bounding adsorption evaluation criteria values represent fundamental physical limits remains a conjecture at this point.

4. Conclusion

We have simulated CO_2 , CH_4 , and N_2 adsorption in over 130 000 hypothetical MOFs and subsequently assessed their usefulness for CO_2 separations applications *via* five adsorbent evaluation criteria. The resulting structure–property relationships, which include pore size, surface area, pore volume, and chemical functionality, are sharply defined and provide, in our view, the clearest guide to experimental synthesis thus reported in the literature. Although none of the evaluation criteria considered are perfect predictors of CO_2 separation performance, our analysis nevertheless provides several leads for future porous material design.

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