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Carbon Dioxide Capture

Development and Evaluation of Porous Materials for Carbon Dioxide Separation and Capture

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The development of new microporous materials for adsorption separation processes is a rapidly growing field because of potential applications such as carbon capture and sequestration (CCS) and purification of clean-burning natural gas. In particular, new metal-organic frameworks (MOFs) and other porous coordination polymers are being generated at a rapid and growing pace. Herein, we address the question of how this large number of materials can be quickly evaluated for their practical application in carbon dioxide separation processes. Five adsorbent evaluation criteria from the chemical engineering literature are described and used to assess over 40 MOFs for their potential in CO_2 separation processes for natural gas purification, landfill gas separation, and capture of CO_2 from power-plant flue gas. Comparisons with other materials such as zeolites are made, and the relationships between MOF properties and CO_2 separation potential are investigated from the large data set. In addition, strategies for tailoring and designing MOFs to enhance CO_2 adsorption are briefly reviewed.

1. Introduction

1.1. Needs for CO_2 Separation and Capture

The concentration of CO_2 in the atmosphere has increased rapidly in recent decades, and many people are greatly concerned about its effect on the environment. The 2007 Assessment Report of the Intergovernmental Panel on Climate Change estimated that the CO_2 concentration in the Earth's atmosphere is the most significant contribution to global warming among all of the Earth's radiative-forcing components.[1] CO_2 capture and sequestration (CCS) is thus currently a very active research area, because CCS could provide a mid-term solution allowing humanity to continue using fossil energy until renewable energy technologies mature.[2] Before CO_2 can be sequestrated it must be separated and captured from the major sources. Flue gas emissions of power plants are responsible for roughly 33–40% of total CO_2 emissions.[2,3] As the major component of the flue gas is nitrogen (>70%) and the major impurity is CO_2 (10–15%), CCS will require the separation of CO_2 from nitrogen.

Another energy-related separation involving CO_2 is removal of CO_2 from natural gas. Demand for natural gas is expected to increase continuously in the coming years, because natural gas produces lower CO_2 emissions than other fossil fuels. In fact, the demand for natural gas may exceed that for coal by 2020.[4] Natural gas is mainly composed of methane, typically 80–95%, with impurities such as CO_2, nitrogen, and heavier hydrocarbons, depending on the source of the gas. In addition, methane from landfill gas is a rapidly growing source of natural gas; however, it often contains unacceptable levels of contaminants. A typical municipal or industrial landfill gas consists of approximately 40–60% CO_2.[5] The separation of CO_2 from methane is essential for the upgrading of natural gas and the treatment of landfill gas to improve purity and reduce pipeline corrosion induced by acid CO_2 gas.[6]

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1.2. Current CO_2 Separation Technologies

Three main approaches have been proposed for the separation of CO_2/CH_4 and CO_2/N_2 mixtures: absorption with liquid solvents, membranes, and adsorption using porous solids. Currently, the most widely adopted approach is absorption using aqueous amine solutions (e.g. monoethanol amine), and this technology has been used in the natural gas industry for more than 60 years.[2] The aqueous basic solvents selectively absorb the mildly acidic CO_2 under ambient conditions. Then, the solvent is regenerated by heating the solution at temperatures well above 100 °C. This requires a substantial amount of energy.[7] Thus, research is still in progress to develop better solvents that require less heating for regeneration and are able to absorb more CO_2.[8,9]

Membranes have been extensively studied for CO_2 separation because of their high selectivity, their low energy requirements, and their simplicity.[10] Although membranes are promising for bulk CO_2 separation processes at elevated pressures, they are not likely to be the most efficient approach for treating mixtures with low CO_2 partial pressure because additional energy is needed to compress the feed gas.[10,11]

Adsorption using porous materials has also been widely used for separating CO_2 from various sources. The two main methods for configuring an adsorption process are pressure-swing adsorption (PSA) and temperature-swing adsorption (TSA). In a PSA process, the adsorbent is regenerated by lowering the pressure, whereas in a TSA process, the regeneration is carried out by increasing the temperature.[12] Although TSA is more effective in cleaning the adsorbent, it has the disadvantage of relatively slow heating and cooling steps. For this reason, TSA is limited to the removal of small quantities of strongly adsorbed impurities.[13] Because of the low energy requirement and fast regeneration,[8] PSA is now used as a commercial technology for a number of applications. If the regeneration pressure is less than 1 atm, the process is referred to as vacuum-swing adsorption (VSA). For flue gas separation processes, VSA is considered to be more promising than regular PSA because pressurizing the large feed stream is cost prohibitive.[7]

Various adsorbents have been considered for CO_2 separation and capture, including microporous and mesoporous materials (activated carbon, carbon molecular sieves, zeolites, and chemically functionalized mesoporous materials), metal oxides, and so on.[10] However, currently available adsorbents are not selective enough for CO_2 separation from flue gases because they also adsorb considerable amounts of N_2.[8] Thus, research on adsorption focuses on developing highly selective adsorbents with high CO_2 capacities.

1.3. MOFs as New Porous Materials for CO_2 Separation and Capture

Metal-organic frameworks (MOFs)—also known as porous coordination polymers—are a new class of crystalline porous materials that have attracted considerable attention because of their unique structural properties, including high-surface area (up to $6200\ \mathrm{m^2g^{-1}}$), high porosity (up to 90 %), and low crystal density, as well as high thermal and chemical stability.[10,14,15] MOFs consist of metal or metal oxide corners connected by organic linkers and are synthesized in a self-assembly process from these well-defined building blocks (Figure 1). The major advantage of MOFs over more traditional porous materials, such as zeolites or carbon-based

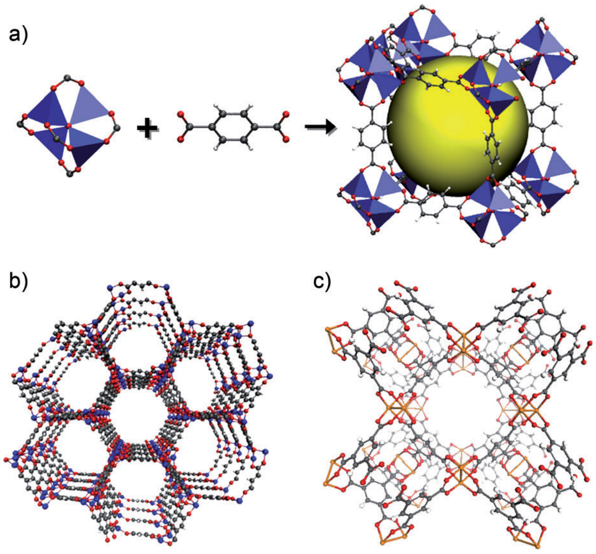

Figure 1. a) Assembly of a MOF (IRMOF-1) by the modular synthesis of metal oxide corners (Zn_4O) and organic linkers (benzenedicarboxylic acid), b) Mg-MOF-74, and c) HKUST-1.

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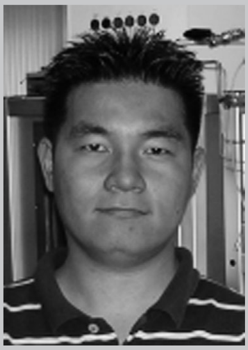

Youn-Sang Bae received his PhD in Chemical Engineering in 2006 at Yonsei University (Korea), under the supervision of Prof. C.-H. Lee, in the field of adsorptive separation process. Following postdoctoral work with Prof. Snurr, he was promoted to research assistant professor at Northwestern University in 2010. His research involves experimental and computational studies of metal-organic framework materials for energy storage and various separation processes.

adsorbents, is the greater scope for tailoring these materials for specific applications because of the modular synthesis.[14,16] By choosing appropriate building blocks, solids with cavities of pre-defined shapes and functionalities can be created to provide optimal host/guest interactions. To date, there are tens of thousands of MOFs catalogued in the Cambridge Structural Database (CSD), and many of them are porous and stable upon solvent removal. However, this is only a tiny fraction of imaginable materials because of the large variety of possible linker and corner units and the possibility to modify MOFs after their synthesis. The family of MOFs includes subsets such as isoreticular MOFs (IRMOFs),[17] zeolitic imidazolate frameworks (ZIFs),[18] and zeolite-like MOFs (ZMOFs).[19] Moreover, although covalent organic frameworks (COFs)[20] and porous organic polymers (POPs)[21] are not strictly MOFs, they are similar classes of materials because they are also made from building-block approaches. Herein, we include all types of MOFs, as well as COFs and POPs.

Currently, research efforts towards industrial applications of these materials include gas storage,[22] gas separation,[23,24] and heterogeneous catalysis.[25] In particular, investigation of these materials for CO_2 separation and capture has become very active in the past few years.[10,11,23]

1.4. Objectives

Given the rapidly growing number of new adsorbents, a critical question is how these materials can be quickly evaluated for their applicability in CO_2 separation processes. This is the main focus of this Minireview. We describe five adsorbent evaluation criteria from the engineering literature and use them to evaluate over 40 MOFs for their potential in CO_2 separation and capture. We also include several POPs, zeolites, and activated carbon. Finally, from the large data set assembled, we investigate the relationships between adsorbent properties and CO_2 separation and capture abilities. We start by first summarizing several strategies that have been used to design MOFs for CO_2 separation processes.

2. Strategies for Improving MOFs for CO_2 Separation and Capture

To date, many attempts have been reported for improving the ability of MOFs to selectively adsorb CO_2. Here, we briefly review these strategies, focusing on four categories: pore-size control, open metal sites, polar functional groups, and introduction of alkali-metal cations. A more detailed discussion of this topic is provided in a recent review by D'Alessandro et al.[10]

2.1. Pore-Size Control

One of the most important factors for gas adsorptive separation processes by microporous materials is pore size. When the pore size of a material is located between the kinetic diameters of two gas molecules (e.g. CO_2: 3.3 Å; CH_4: 3.8 Å), one can separate the two gases by a molecular sieving effect (or a steric effect). If the pores are the right size, only the smaller molecule (CO_2) can diffuse into the pores, whereas the larger molecule (CH_4) is totally excluded. If the pore size is slightly larger than the kinetic diameter of the larger molecule (CH_4), one can separate the two gases by a kinetic separation, which is achieved by the difference in the diffusion rates. In this case, the larger molecule (CH_4) diffuses slower than the smaller molecule (CO_2). When the pore size is large enough that both molecules can readily diffuse into the pores, the two molecules may be separated by differences in their equilibrium adsorption, which is used in a large majority of adsorptive separation processes. Even for separation processes based on differences in equilibrium adsorption, the pore size may play a role in dictating the amount adsorbed. In most cases, pores that are too large do not show good gas separation properties.

Several MOFs have shown selective adsorption of CO_2 over N_2 or CH_4 by the molecular sieving effect,[26–29] and a few MOFs have exhibited selective CO_2 adsorption by the kinetic separation effect.[30,31] Other than these cases, most reports of selective CO_2 adsorption in MOFs are because of differences in the equilibrium adsorption, in which the relative interactions between the adsorbate (CO_2, CH_4, or N_2) and the MOF atoms are most important.

2.2. Open Metal Sites

Metal atoms in most MOFs are coordinatively saturated by framework components, but in some MOFs some of the metal atoms are partially coordinated by guest solvent molecules. When these coordinated solvent molecules are removed by heating the material, coordinatively unsaturated metal sites are created within the MOF pores.[32,33] These open metal sites have been widely studied for improving H_2 storage in MOFs and increasing the heat of adsorption (Q_{st}) of H_2.[34] They have also been shown to be promising for improved CO_2 capture and separation. For example, Bae et al. compared the CO_2/CH_4 selectivities between carborane-based MOFs with and without open metal sites, and the results suggested that open metal sites in a MOF can aid in the separation of (quadru)polar/nonpolar pairs such as CO_2/CH_4.[32]

A series of isostructural frameworks $[M_2(dhtp)(H_2O)_2]$ (H_4dhtp: 2,5-dihydroxyterephthalic acid; M = Zn, Ni, Co, Mg, Mn) with 1D-hexagonal channels of around 11 to 12 Å were shown to have high concentrations of open metal sites after the removal of coordinated H_2O molecules. These MOFs are also denoted M-MOF-74,[35] CPO-27-M,[36] and M/dobdc[37] ($dobdc^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate). This series of MOFs showed high CO_2 uptake especially at low pressures (0.1–0.2 bar), which is the pressure region of interest in flue gas separation.[36,37] Also, these MOFs have high Q_{st} values for CO_2 (37–47 $kJ\,mol^{-1}$), which suggests preferential adsorption of CO_2 on open metal sites.[36,37] To confirm this, Dietzel et al. obtained an X-ray single-crystal structure of CO_2 bound "end-on" to the open metal sites in Ni-MOF-74, which clearly shows the role of the open metal sites in CO_2 binding.[38] Hence, these MOFs are considered some of the most promising MOFs for CO_2 capture and separation. Another interesting feature of these MOFs is that they can be made with different metals; among this series, the MOF with Mg showed the highest CO_2 uptake as well as the highest Q_{st} value for CO_2.[37] Yazaydin et al. noted that one reason why M-MOF-74 MOFs show better CO_2 adsorption than other MOFs containing open metal sites is the higher density of open metal sites in M-MOF-74.[39] Many other MOFs with open metal sites also have shown considerable CO_2/CH_4 or CO_2/N_2 selectivities, although they do not show such high CO_2 uptakes as are observed in M-MOF-74.[29,40–43]

2.3. Polar Functional Groups

One of the most attractive properties of MOFs is the possibility to tailor the pore structure and functionality by exploiting the richness of organic chemistry. Efforts to tune the pore size and provide desired surface properties of MOFs can be divided into two main strategies: 1) direct assembly and 2) post-synthesis modification.[44]

The first strategy is the direct assembly of new MOFs from particular metal nodes and organic linkers with specific functionalities. As an example, Yaghi and co-workers synthesized a series of zeolitic imidazolate frameworks (ZIFs) with the gmelinite (zeolite code GME) topology.[45] By changing the imidazole linker, they produced a wide range of pore metrics and functionalities for CO_2 separation processes. The imidazole link functionality was altered from polar ($-NO_2$, ZIF-78; $-CN$, ZIF-82; $-Br$, ZIF-81; $-Cl$, ZIF-69) to nonpolar ($-C_6H_6$, ZIF-68; $-CH_3$, ZIF-79). The order of CO_2 uptake at 1 bar and 298 K was in line with the greater attractions expected between the polar functional groups in the ZIFs and the strongly quadrupolar CO_2. Also, ZIF-78 and ZIF-82 showed higher CO_2/CH_4, CO_2/N_2, and CO_2/O_2 selectivities than the other ZIFs because the $-NO_2$ and $-CN$ groups in these ZIFs have greater dipole moments than the other functional groups. These results suggested that highly polar functional groups are helpful for attaining high CO_2 selectivities as well as high CO_2 uptake. Another attractive feature of the ZIFs for practical application is their high chemical and thermal stability.

Another example of direct assembly of new MOFs is the cobalt–adenine MOF named bio-MOF-11. Rosi and co-workers synthesized this MOF based on the idea that the multiple Lewis basic sites of adenine, including an amino group and pyrimidine nitrogens, should have a strong interaction with CO_2.[28] The gas adsorption results showed high CO_2 uptake at 298 K and very minor N_2 adsorption. Also, this material showed a high Q_{st} value for CO_2 (around 45 kJ mol^{-1}), which is similar to values for some other amine-functionalized MOFs. They explained the large CO_2/N_2 selectivity and high Q_{st} value for CO_2 by the combined effects of molecular sieving and the highly polar functional groups in the pores. Similarly, amine-functionalized MIL-53(Al) showed a significant increase in the CO_2/CH_4 separation factor (from 5 to 60) compared to the nonfunctionalized MOF.[46] In addition, the amine-MIL-53(Al) showed a much higher Q_{st} value for CO_2 (around 38.4 kJ mol^{-1}) than the parent MIL-53(Al) (< 20 kJ mol^{-1}).

In the above direct-assembly strategies, certain functional groups may be hard to incorporate into MOFs, either because of instability under conditions for MOF synthesis or because of competitive reaction with intended framework components.[47] The other strategy for controlling the pore size and creating desired functionalities in MOFs is the post-synthesis modification of pre-constructed, robust precursor MOFs.[44] For example, Farha et al. synthesized a series of cavity-modified MOFs by replacing coordinated solvents with several different pyridine ligands.[47] Among them, a p-$(CF_3)NC_5H_4$-modified MOF showed considerable improvements in the CO_2/N_2 and CO_2/CH_4 selectivities compared to the unmodified parent MOF.[31] This was attributed to the highly polar $-CF_3$ functional groups as well as the constricted pores of the modified MOF (Figure 2). This suggests that post-synthesis modification of MOFs by replacing coordinated solvent molecules with highly polar ligands may be a powerful method for generating new MOFs for CO_2 separation processes.

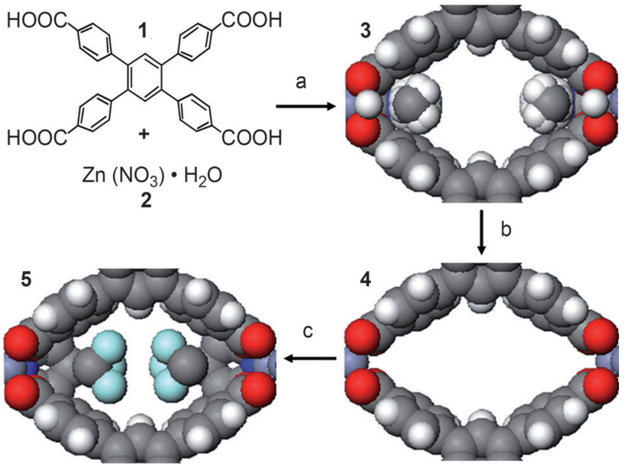

Figure 2. An example of post-synthesis modification. First, the MOF is synthesized in DMF, and noncoordinated solvent molecules are removed by evacuation during heating at 100 °C to yield **3**, in which the coordinated DMF molecules remain. In step b, the material is heated at 150 °C to remove the coordinated DMF molecules and open metal sites in **4** are created. In step c, **4** is soaked in a solution of $CHCl_3$/4-(trifluoromethyl)pyridine, followed by evacuation during heating at 100 °C.[31] Reproduced with permission from The Royal Society of Chemistry.

In another post-synthesis modification, Long and co-workers grafted an alkylamine functionality onto open metal sites of a triazolate-bridged MOF.[48] Compared to the parent MOF, the ethylenediamine-functionalized MOF exhibited a steeper CO_2 isotherm at very low pressures, although it showed considerably reduced CO_2 uptake at high pressures. Also, the ethylenediamine-functionalized MOF exhibited very high Q_{st} values for CO_2 (around 90 kJ mol^{-1}) at low surface coverage, which indicates a strong chemical interaction of CO_2 with the alkylamine functionalities. As the available alkylamine groups bind CO_2 with increasing pressure, Q_{st} decreased rapidly, approaching the values observed for the nonfunctionalized MOF (around 21 kJ mol^{-1}). Remarkably, despite the reduction in CO_2 capacity upon grafting of alkylamine, the alkylamine functionalities endow the material with a higher CO_2/N_2 selectivity over the entire pressure range measured (up to 1.1 bar).

In the above examples, the post-synthesis modifications were done using coordinatively unsaturated metal sites. However, post-synthesis modifications can be also performed through the organic ligands. Cohen and Wang did a systematic investigation on the post-synthesis modification of MOFs through covalent transformations of amino groups on the linkers.[44] Although they did not investigate CO_2 separation processes using post-synthetically modified MOFs, this kind of post-synthesis modification should be useful for the design of new MOFs for CO_2 separation processes.

2.4. Extraframework Cations

Incorporating lithium ions into MOFs has attracted considerable interest because of the potential for obtaining high Q_{st} values for H_2.[49] Mulfort et al. demonstrated two strategies for incorporating Li cations into MOFs. One is chemical reduction of a MOF with Li metal,[50] and the other is exchange of a hydroxyl proton in a MOF linker for a Li cation.[51] Both methods brought considerable enhancements in H_2 uptake. Later, Farha et al. showed that chemical reduction can enhance the CO_2/CH_4 selectivity in a diimide-based porous organic polymer (POP).[52] In addition, Bae et al. have recently shown that incorporation of Li cations into MOFs by either of the two methods, chemical reduction or cation exchange, significantly improves the CO_2/CH_4 selectivity.[53] In a similar fashion, zeolite-like MOFs (ZMOFs)[19,54] that contain extraframework ions should be promising for CO_2 separation processes. Recently, a computational study predicted that *rho*-ZMOF, which contains an anionic framework and charge-balancing extraframework Na^+ ions, should display highly selective CO_2 adsorption over H_2, CH_4, and N_2.[55]

3. Evaluation of MOFs for CO_2 Separation and Capture

Short of operating a full PSA process, the best way to evaluate MOFs for large-scale CO_2 separation and capture is probably to test the materials under mixture conditions by measuring the column dynamics from breakthrough measurements, and a few MOFs have been already tested by this packed-column method.[46,56,57] However, these breakthrough measurements require a specially designed experimental system. Measurements of equilibrium mixture isotherms sound straightforward but are tedious in practice and require additional measurements for determining the compositions of both gas and adsorbed phases.[12] Thus, until now, most studies on CO_2 separation and capture using MOFs have reported single-component isotherms of CO_2, CH_4, and N_2. To date, a large number of single-component CO_2 isotherms in MOFs under ambient conditions have been reported and were well summarized in a recent review.[23] But, for CH_4 and N_2, only a relatively small number of isotherms have been reported at ambient temperatures, the industrially interesting condition.

Based on these limited data, many MOFs have been suggested to be promising for CO_2 capture and separation processes. However, CO_2 uptake is not enough to evaluate materials for use in real pressure-swing adsorption or vacuum-swing adsorption processes. What is needed are simple criteria for evaluating different adsorbents. These criteria should take into account mixture conditions and the cyclic nature of the PSA processes.

The adsorption selectivity of component 1 over component 2 (α_{12}), defined as the ratio of the equilibrium uptakes in the pore to the ratio of the molar fractions of the bulk phase, has been widely used as an adsorbent evaluation criterion for various separation processes. By convention, component 1 is the more strongly adsorbed component. A simple method for determining the adsorption selectivity is to take the ratio of the Henry's law constants, but this is guaranteed to reflect the true mixture selectivity only at very low pressure and low loading on the adsorbent.[58] In many studies, the CO_2/CH_4 or CO_2/N_2 selectivities have been calculated for equimolar mixtures, but the selectivities should also be obtained for industrially interesting mixture compositions. A more accurate prediction of adsorption selectivity from single-component isotherms can be obtained by the ideal adsorbed solution theory (IAST).[59] But, surprisingly, only a few research groups use this method.

The adsorption selectivity is not a perfect adsorbent evaluation criterion because it does not reflect the cyclic PSA and VSA processes. Another important parameter for PSA and VSA separation is the working capacity, ΔN, which is defined as the difference between the adsorbed amounts at the adsorption pressure and the desorption pressure. Strictly speaking, the working capacity should be calculated from mixture adsorption data. However, as the experimental measurement of mixture adsorption is rather complicated, single-component isotherms are usually used to calculate the working capacity.[58]

Notaro et al. proposed an "Adsorption Figure of Merit (AFM)", which was empirically derived for the separation of nitrogen from air.[60] This AFM is defined as $(\alpha_{12}^{ads})^2/(\alpha_{12}^{des})$ multiplied by the working nitrogen capacity (ΔN_1). The use of the term $(\alpha_{12}^{ads})^2/(\alpha_{12}^{des})$ may be because the selectivity during the adsorption step (α_{12}^{ads}) is more important than during the desorption step (α_{12}^{des}).[58]

Rege and Yang suggested a sorbent selection parameter, S, that also combines the adsorption selectivity and the working capacity: $S = (\Delta N_1/\Delta N_2)\,\alpha_{12}$.[61] Here, they used a ratio of the working capacities of the two components rather than simply using the working capacity of the strongly adsorbed component, because this seems to be more useful for the evaluation of a cyclic PSA and VSA process. For Langmuir adsorption, α_{12} is equivalent to the ratio of the initial slopes of the isotherms of the two components, that is, the ratio of Henry-law constants. However, for non-Langmuir systems, α_{12} should be replaced by $(\alpha_{12}^{ads})^2/(\alpha_{12}^{des})$, as given by the AFM of Notaro et al.

The regenerability, R, may also be an important factor in cyclic PSA and VSA processes. This parameter is defined as the ratio of the working capacity and the adsorbed amount at the adsorption pressure. It represents the fraction of the adsorption sites that are regenerated during the desorption step.[62]

3.1. *Adsorbent Evaluation Criteria*

Five adsorbent evaluation criteria are used herein to assess a large number of MOFs from the literature for their applicability in CO_2 separation processes. The five adsorbent evaluation criteria are:

1) CO_2 uptake under adsorption conditions (mol kg^{-1}), N_1^{ads}
2) Working CO_2 capacity (mol kg^{-1}), $\Delta N_1 = N_1^{ads} - N_1^{des}$
3) Regenerability (%), $R = (\Delta N_1 / N_1^{ads}) \times 100$
4) Selectivity under adsorption conditions, $\alpha_{12}^{ads} = (N_1^{ads}/N_2^{ads})(y_2/y_1)$
5) Sorbent selection parameter, $S = (\alpha_{12}^{ads})^2/(\alpha_{12}^{des})(\Delta N_1/\Delta N_2)$

Here, N is the adsorbed amount and y is the molar fraction in the gas phase. Subscripts 1 and 2 indicate the strongly adsorbed component (CO_2) and the weakly adsorbed component (CH_4 or N_2), respectively. Superscripts ads and des mean adsorption and desorption conditions, respectively.

These evaluation criteria can be used to quickly evaluate materials for use in real PSA and VSA processes. It should be noted here that none of these criteria are perfect but the criteria are complementary with each other. Because only single-component isotherms of two gases at appropriate pressure and temperature ranges are required, these criteria can be easily calculated by material chemists to evaluate new materials. We use these criteria to assess over 40 MOFs and POPs from the literature (for the cases that both CO_2 and CH_4 isotherms or both CO_2 and N_2 isotherms were reported at room temperature) for their potential in four possible PSA and VSA applications: 1) natural gas purification using PSA; 2) landfill gas separation using PSA; 3) landfill gas separation using VSA; 4) flue gas separation using VSA.

In our evaluation, simulation data are not included but only experimental data are considered. All of the adsorbed amount values (N_1^{ads}, N_1^{des}, N_2^{ads}, and N_2^{des}) are taken from tables or listed values if possible. If such data are not available, these values are obtained from scanned plots using ScanIt 1.0 software. Also, the isotherms that do not contain enough data points at the pressures of interest are excluded. Some promising MOFs are not included in our evaluations since experimental gas isotherms at the pressure and temperature ranges of interest are not available.

3.2. *Case 1: Natural Gas Purification Using PSA*

First, we evaluate materials for natural gas purification using PSA. For this evaluation, we assume that the typical composition of natural gas is $CO_2/CH_4 = 10{:}90$ and the typical adsorption and desorption pressures of a PSA process are 5 and 1 bar, respectively (Table 1). All the adsorbed amount values under adsorption and desorption conditions are obtained at the partial pressure of the specific component. For example, N_1^{ads} is obtained at 0.5 bar, which is the partial pressure of CO_2 under adsorption condition. For case 1, 21 MOFs and 3 POPs are evaluated together with three commercially used adsorbents (zeolite-13X, zeolite-5A, and activated carbon). Full evaluation results for all four cases are reported in Table S1 in the Supporting Information.

Table 1: Mixture compositions and pressures for four case studies.

	Mixture composition	Adsorption and desorption pressures (p^{ads} and p^{des})
Case 1	$CO_2/CH_4 = 10{:}90$	$p^{ads} = 5$ bar, $p^{des} = 1$ bar
Case 2	$CO_2/CH_4 = 50{:}50$	$p^{ads} = 5$ bar, $p^{des} = 1$ bar
Case 3	$CO_2/CH_4 = 50{:}50$	$p^{ads} = 1$ bar, $p^{des} = 0.1$ bar
Case 4	$CO_2/N_2 = 10{:}90$	$p^{ads} = 1$ bar, $p^{des} = 0.1$ bar

Table 2 lists the top candidates for case 1 in terms of the S value, which reflects the cyclic nature of the PSA process. Interestingly, 55% Li-reduced diimide-POP and amine-MIL-53(Al) have very high S values although they do not show large N_1^{ads} and ΔN_1 values. This is because they have relatively high working capacity ratios ($\Delta N_1/\Delta N_2$). This can be explained by the presence of polar functional groups in these MOFs that prefer quadrupolar CO_2 to nonpolar methane. 55% Li-reduced diimide-POP has chemically reduced ligands as well as high charge density at the oxygen sites. Amine-MIL-53(Al) has polar amino and hydroxyl groups, leading to increased CO_2 uptake. Also, amino groups in this MOF reduce apolar adsorption sites on the aromatic ring of the linker, leading to reduced CH_4 uptake.[46] Remarkably, two MOFs and two Li-reduced POPs show higher sorbent selection parameters (S) than the zeolites and activated

Table 2: Top candidates for natural gas purification using PSA (case 1) among MOFs and POPs evaluated.[a]

Adsorbent, temperature	N_1^{ads}	ΔN_1	R	α_{12}^{ads}	S	Reason[b]
55% Li-reduced diimide-POP, 298 K[52]	1.11	0.63	**56.3**	16.1	**21.4**	D, E
Amine-MIL-53(Al), 303 K[46]	0.89	0.62	**69.7**	16.7	**18.7**	E
35% Li-reduced diimide-POP, 298 K[52]	1.49	0.91	**61.0**	11.6	**11.8**	D, E
HKUST-1, 298 K[42]	2.70	**1.70**	**63.0**	10.0	**9.6**	C
Zeolite-13X, 298 K[5]	*3.97*	*1.48*	*37.3*	*18.9*	*9.0*	*D*
Diimide-POP, 298 K[21]	1.39	0.86	**62.2**	9.7	7.5	E
[Zn_2(tcpb){p-(CF_3)NC_5H_4}$_2$], 298 K[31]	0.46	0.30	**64.7**	7.3	5.7	B, E

[a] Bold numbers indicate that some materials surpass zeolites. [b] A: simple physical interaction; B: pore size effect; C: open metal sites; D: alkali-metal cations and framework reduction; E: polar functional groups.

carbon. In terms of the α_{12}^{ads} value, however, zeolite-5A (20.0) and zeolite-13X (18.9) seem to be superior to all of the MOFs evaluated. Nevertheless, Mg-MOF-74, amine-MIL-53(Al), and 55 % Li-reduced diimide-POP show high α_{12}^{ads} values (17.3, 16.7, and 16.1), which are close to the values for the zeolites (see Table S1 in the Supporting Information). In addition, most of the MOFs and POPs have much better regenerability than zeolites because they have rather modest isotherms at low pressures. However, Mg-MOF-74 and Ni-MOF-74 show rather low regenerability (20.7 and 30.3 %) because of the strong interaction of CO_2 with open metal sites. Nevertheless, Mg-MOF-74 and Ni-MOF-74 show much larger N_1^{ads} values (7.23 and 6.23 mol kg^{-1}) than zeolite-13X, zeolite-5A, and activated carbon (3.97, 3.80, and 1.40 mol kg^{-1}). Moreover, Ni-MOF-74, HKUST-1, and Mg-MOF-74 show larger ΔN_1 values (1.89, 1.70, and 1.50 mol kg^{-1}) than zeolite-13X, zeolite-5 A, and activated carbon (1.48, 0.52 and 1.02 mol kg^{-1}). Interestingly, all three MOFs that exhibit large N_1^{ads} and ΔN_1 values have open metal sites in the pores.

3.3. Case 2: Landfill Gas Separation Using PSA

The typical composition of landfill gas, that is, the CO_2/CH_4 ratio, is assumed to be 50:50, and the typical adsorption and desorption pressures of a PSA process are again taken to be 5 and 1 bar (Table 1). For case 2, 21 MOFs and 3 POPs are evaluated and compared with zeolite-13X, zeolite-5A, and activated carbon (see Table S1 in the Supporting Information).

In Table 3, the top candidates for landfill gas separation in terms of the *S* value are listed. Remarkably, more than ten MOFs and POPs have much higher *S* values than zeolites (zeolite-13X: 2.0, zeolite-5A: 0.6) and activated carbon (3.6). In addition, in terms of the selectivity α_{12}^{ads}, MIL-101c, HKUST-1, and 55 % Li-reduced diimide-POP surpass the zeolites (zeolite-13X: 4.2, zeolite-5A: 3.4) and activated carbon (2.0). These results indicate that MOFs and POPs can be good candidates for landfill gas separation using PSA. Among the materials evaluated, HKUST-1 and MIL-101c seem to be the most promising MOFs considering all of the adsorbent evaluation criteria. Both of these MOFs have open metal sites as well as large pore volumes. Moreover, MOFs possessing open metal sites (Mg-MOF-74, Ni-MOF-74, HKUST-1 and MIL-101c) show considerably larger N_1^{ads} and ΔN_1 values than zeolites and activated carbon. However, Mg-MOF-74 and Ni-MOF-74, which have a high density of open metal sites, show low regenerabilities (28.7 and 26.5 %, respectively) because of the steep isotherms at low pressures. MOFs with lower densities of open metal sites, HKUST-1 and MIL-101c, show relatively high regenerabilities. Similar to case 1, most of the MOFs and POPs have much better regenerability than zeolites.

Table 3: Top candidates for landfill gas separation using PSA (case 2) among MOFs and POPs evaluated.[a]

Adsorbent, temperature	N_1^{ads}	ΔN_1	R	α_{12}^{ads}	S	Reason[b]
HKUST-1, 298 K[42]	**8.01**	**5.34**	**66.7**	**4.9**	**21.0**	C
35 % Li-reduced diimide-POP, 298 K[52]	2.93	**1.44**	**49.2**	3.6	**11.5**	D, E
MOF-508b, 303 K[56]	3.60	**2.58**	**71.7**	2.9	**10.9**	A
MIL-101c, 303 K[43]	**6.70**	**3.20**	**47.8**	**5.0**	**9.5**	C
$[Zn_3(OH)(p\text{-}cdc)_{2.5}(dmf)_4]$, 298 K[32]	0.94	0.66	**70.6**	3.3	**8.3**	A
55 % Li-reduced diimide-POP, 298 K[52]	2.12	1.01	**47.5**	**4.6**	**7.7**	D, E
Zeolite-13X, 298 K[5]	*5.37*	*1.40*	*26.1*	*4.2*	*2.0*	*D*

[a] Bold numbers indicate that some materials surpass zeolites. [b] See Table 2.

3.4. Case 3: Landfill Gas Separation Using VSA

In case 2, we examined the separation of landfill gas (an equimolar mixture of CO_2 and CH_4) as performed by a PSA process that is operated between 5 and 1 bar. However, this separation can also be reached by a VSA process, which is typically operated between 1 and 0.1 bar (Table 1). For case 3, 27 MOFs and 3 POPs are evaluated and compared with commercially available adsorbents (see Table S1 in the Supporting Information).

For case 3, several MOFs, including CUK-1, Mg-MOF-74, $[Zn_3(OH)(p\text{-}cdc)_{2.5}]$ (p-cdc = deprotonated form of 1,12-dihydroxydicarbonyl-1,12-dicarba-closo-dodecarborane), Ni-MOF-74, ZIF-82, and HKUST-1, have higher *S* values than zeolites (Table 4). In particular, CUK-1 shows a particularly high *S* value, which arises from a low working capacity of CH_4 (ΔN_2). Moreover, CUK-1 has a slightly higher α_{12}^{ads} value than zeolite-13X. In addition, all the MOFs listed as top candidates in terms of the *S* value have open metal sites (Mg-MOF-74, $[Zn_3(OH)(p\text{-}cdc)_{2.5}]$, Ni-MOF-74, and HKUST-1) or polar functional groups (CUK-1: μ_3-OH, ZIF-82: -CN). This indicates that MOFs with strong energetic sites are

Table 4: Top candidates for landfill gas separation using VSA (case 3) among MOFs and POPs evaluated.[a]

Adsorbent, temperature	N_1^{ads}	ΔN_1	R	α_{12}^{ads}	S	Reason[b]
CUK-1, 298 K[26]	2.76	**2.33**	**84.4**	**14.0**	**359**	B, E
Mg-MOF-74, 298 K[36]	**7.23**	**2.32**	32.1	12.5	**23.5**	C
$[Zn_3(OH)(p\text{-}cdc)_{2.5}]$, 298 K[32]	0.59	0.49	**83.1**	7.8	**21.4**	C
Ni-MOF-74, 298 K[36]	**6.23**	**3.16**	**50.7**	8.5	**21.0**	C
ZIF-82, 298 K[45]	1.42	1.20	**84.9**	5.6	**20.5**	E
HKUST-1, 298 K[41,42]	2.81	1.90	**67.5**	5.5	**19.8**	C
Zeolite-13X, 298 K[5]	*3.97*	*1.97*	*49.6*	*13.2*	*19.1*	*D*

[a] Bold numbers indicate that some materials surpass zeolites. [b] See Table 2.

promising for landfill gas separation using VSA. An interesting point is that the top candidates are totally different between cases 2 and 3 even though both cases address the same landfill gas separation focusing on the equimolar CO_2/CH_4 mixture. The only difference between cases 2 and 3 is the operating pressure. This implies that we need to match the material and process and that we cannot simply state that one material is better in general than another for a given separation process.

Similar to cases 1 and 2, Mg-MOF-74 and Ni-MOF-74 have large N_1^{ads} and ΔN_1 values but also rather low regenerabilities because of their high densities of open metal sites. Although CUK-1 and HKUST-1 show lower N_1^{ads} values than zeolite-13X, they give a larger or a similar ΔN_1 value compared to zeolite-13X.

3.5. Case 4: Flue Gas Separation Using VSA

In cases 1–3, we evaluated adsorbents for three different CO_2/CH_4 separation processes. In case 4, MOFs are evaluated for CO_2/N_2 separation, focusing on flue gas separation, which is currently an important research area. A VSA process is selected here because, for flue gas separation processes, VSA is considered to be more promising than TSA.[7] The typical composition of flue gas, that is, the CO_2/N_2 ratio is assumed to be 10:90 and the adsorption and desorption pressures are set to 1 and 0.1 bar, respectively (Table 1). For case 4, 25 MOFs are evaluated and compared with commercially available adsorbents (see Table S1 in the Supporting Information).

The top candidates for case 4 in terms of the *S* value are listed in Table 5. Most of the MOFs listed have polar functional groups (ZIF-78: $-NO_2$; ZIF-82: $-CN$; ZIF-81: $-Br$; ethylenediamine-$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$ (H_3BTTri = 1,3,5-tris(1H-1,2,3-triazol-4-yl)benzene): grafted ethylenediamine; $[Zn_2(tcpb)\{p\text{-}(CF_3)NC_5H_4\}_2]$ (tcpb = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene): $-CF_3$) and open metal sites (Ni-MOF-74). This indicates that a strong CO_2-MOF interaction may be the most important factor in flue gas separation using VSA, because a high CO_2 uptake at very low pressures (around 0.1 bar) is required. Nevertheless, a relatively low N_2 uptake is also a non-negligible factor because Ni-MOF-74, the best MOF in terms of CO_2 uptake, does not correspond to the highest α_{12}^{ads} or *S* values. In case 4, zeolite materials seem to be superior to most of the evaluated MOFs considering all of the adsorbent evaluation criteria.

Table 5: Top candidates for flue gas separation using VSA (case 4) among MOFs evaluated.[a]

Adsorbent, 298 K	N_1^{ads}	ΔN_1	*R*	α_{12}^{ads}	*S*	Reason[b]
ZIF-78[45]	0.60	0.58	**96.3**	34.5	**396**	E
Zeolite-5A[63]	*3.50*	*2.36*	*67.4*	*61.8*	*163*	*D*
Zeolite-13X[5]	*2.49*	*1.35*	*54.2*	*86.2*	*128*	*D*
ZIF-82[45]	0.41	0.38	**92.5**	26.4	105	E
Co-carborane MOF-4b[29]	0.07	0.06	**83.8**	**154**	104	B
ZIF-81[45]	0.27	0.25	**93.4**	22.7	101	E
Ni-MOF-74[36]	**4.34**	**3.20**	**73.7**	41.1	83.5	C
ZIF-79[45]	0.26	0.24	**92.9**	21.3	83.0	E
ethylenediamine-$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$[48]	0.45	0.26	57.6	58.4	77.2	E
$[Zn_2(tcpb)\{p\text{-}(CF_3)NC_5H_4\}_2]$[31]	0.16	0.13	**80.7**	43.9	57.9	B, E

[a] Bold numbers indicate that some materials surpass zeolites. [b] See Table 2.

Co-carborane-MOF-4b shows the highest α_{12}^{ads} value because of a very low N_2 uptake under adsorption condition, but the values of N_1^{ads} and ΔN_1 are too low for practical use. Among the MOFs, a series of ZIFs (ZIF-78, ZIF-82, ZIF-81, and ZIF-79) and Ni-MOF-74 seem to be promising for flue gas separation using VSA because they have reasonable working capacities of CO_2 as well as high *S* values. It should be noted that MOF-74 materials with other metals such as Mg-MOF-74 were not evaluated because N_2 isotherms at room temperature are not available for these MOFs.

Similar to the previous cases, Mg-MOF-74 and Ni-MOF-74 show the best properties in terms of N_1^{ads} and ΔN_1 values, and most of the MOFs demonstrate better regenerabilities than zeolites. However, most of the MOFs except the series of MOF-74 materials have much lower N_1^{ads} and ΔN_1 values than zeolites. In case 4, steep CO_2 isotherms at low pressures are required because the pressure of interest is 0.1 bar, that is, the CO_2 partial pressure under adsorption conditions.

4. Relationships between Adsorbent Properties and CO_2 Separation Abilities

Knowing the relationships between adsorbent properties and CO_2 separation abilities is essential for the design of advanced materials for CO_2 separation. Herein, the relationships between adsorbent properties (pore size, surface area, pore volume, and heat of adsorption) and the five adsorbent evaluation criteria are investigated from the large experimental data set that is assembled in Table S1 in the Supporting Information.

For all cases, we could not find any strong correlation between purely structural properties (pore size, surface area, and pore volume) and the five adsorbent criteria (see Figures S1–S3 in the Supporting Information). These observations agree with a recent experimental study by Yaghi and co-workers.[45] They studied the effect of pore size and functional groups on CO_2/CH_4, CO_2/N_2, and CO_2/O_2 separation processes in a series of zeolitic imidazolate frameworks (ZIFs). They reported that CO_2 selectivity does not have any noticeable relationship with pore diameter but rather with functional groups. Also, in a recent simulation study for 14 diverse MOFs, Yazaydin et al. reported that CO_2 uptake at $P < 1$ bar does not show any correlation with surface area and free volume.[39]

From the assembled data, we found several interesting correlations between the heat of adsorption (Q_{st}) of CO_2 and the adsorbent evaluation criteria. Note that Q_{st} is a function of loading, but for simplicity we used the value at the lowest loading reported. The heat of adsorption at low loading reflects mainly the interactions between CO_2 and the sorbent (rather than CO_2/CO_2 interactions). For cases 1, 3, and 4, which have low CO_2 partial pressures (0.1 or 0.5 bar) under adsorption conditions, weak positive correlations between N_1 and Q_{st} values are observed as shown in Figure 3. On the

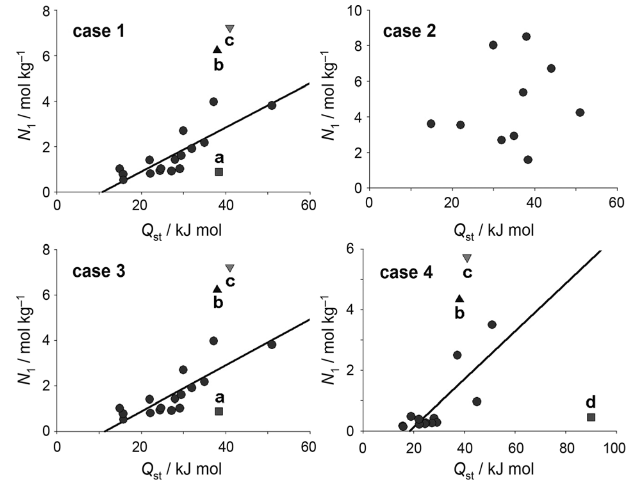

Figure 3. Relationship between N_1 and Q_{st} values for cases 1–4. The MOFs represented by a–d are not included in the linear regression lines (solid lines): a) amine-MIL-53(Al), b) Ni-MOF-74, c) Mg-MOF-74, and d) ethylenediamine-$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$.

other hand, for case 2, which has a relatively high CO_2 partial pressure (2.5 bar) under adsorption conditions, the N_1 value shows no correlation with the Q_{st} value. These results are well explained by a previous report from Frost et al. that, at low pressures, uptake correlates with the Q_{st} value; and at higher pressures, it correlates with the surface area or the free volume.[64] The correlations for cases 1, 3, and 4 are somewhat weak, with notable deviations. For example, several MOFs with high Q_{st} value exhibit only low CO_2 uptake (see cases 1 and 3: amine-functionalized MIL-53(Al) and case 4: ethylenediamine-$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$). In addition, the M-MOF-74 MOFs lie well above the correlation lines. This seems to be related to the high densities of open metal sites in the M-MOF-74 MOFs. Similar efforts to find correlations between the Q_{st} value and CO_2 uptake in MOFs have been reported in two previous studies. Yazaydin et al. reported an excellent correlation between CO_2 uptake and the heat of adsorption at $p < 1$ bar for 14 MOFs.[39] An exception to their correlation was observed for [Pd(2-pymo)$_2$] (2-pymo = 2-hydroxypyrimidinolate), which showed the highest Q_{st} value but yielded only a small CO_2 uptake because of the lower free volume than the other materials. In a recent review article, Keskin et al. presented a figure showing the relationship between the CO_2 uptake in MOFs at 298 K and 1 bar and their Q_{st} values.[23] They concluded that these two quantities are not strongly correlated. In particular, they noted several materials having very high heats of adsorption but low CO_2 uptake. One can easily imagine materials that have low pore volume but very strong sites for CO_2 adsorption. Such materials would not follow the weak correlations seen in Figure 3; see, for example point d for case 4. Nevertheless, it is interesting that for the limited data available, some trends are evident in Figure 3. Additional data for MOFs having higher heats of adsorption would be useful to test the general validity of these observations.

The correlations between working capacity of CO_2 (ΔN_1) and Q_{st} value are similar to those between N_1 and Q_{st} values (see Figure S4 in the Supporting Information). For case 1, however, ΔN_1 does not show any correlation with the Q_{st} value even though there is a weak positive correlation between N_1 and Q_{st} values.

For all cases, the regenerability (R) shows negative correlations with the Q_{st} value as shown in Figure 4 and Figure S5 in the Supporting Information. This is reasonable because, as the Q_{st} value increases, steeper CO_2 isotherms at low pressures are obtained. For steeper isotherms, more CO_2 is adsorbed under adsorption conditions but more CO_2 also remains in the pores under desorption conditions. Hence, the regenerability decreases with increasing Q_{st} value. As the N_1 value shows a weak positive correlation with the Q_{st} value, we can speculate that optimum Q_{st} values may exist for obtaining a high N_1 value with a reasonable regenerability (R) value.

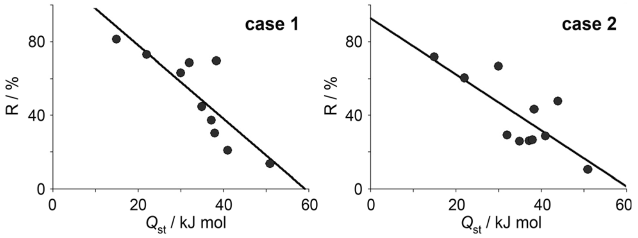

Figure 4. Relationship between regenerability (R) and Q_{st} value for cases 1 and 2. All the data shown are used for the linear regression lines (solid lines). Similar correlations are also observed for cases 3 and 4 (see Figure S5 in the Supporting Information).

The selectivity α_{12}^{ads} shows positive correlations with the Q_{st} value for all cases except case 2, as shown in Figure 5. Interestingly, stronger correlations are observed here than in Figures 3 and 4, but there are still some deviations. Figure 5 suggests that materials with high Q_{st} value generally produce high CO_2 selectivities for CO_2 separation processes, although

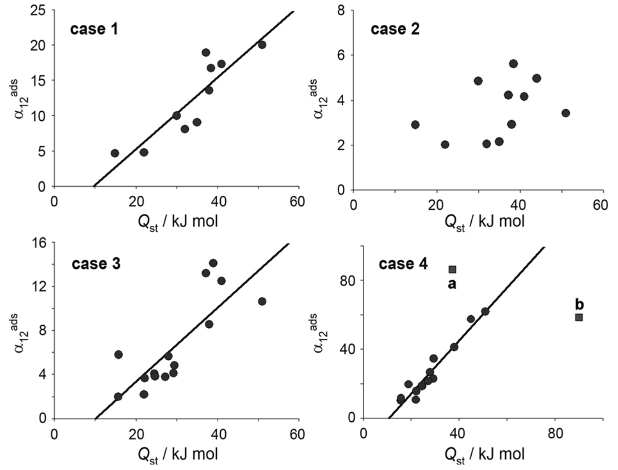

Figure 5. Relationship between selectivity (α_{12}^{ads}) and Q_{st} for cases 1–4. The materials represented by a and b are not included in the linear regression lines (solid lines): a) zeolite-13X and b) ethylenediamine-$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$.

there are exceptions such as case 2. For case 4, zeolite-13X, which has only a moderate Q_{st} value, exhibits the highest selectivity among materials that have reported Q_{st} values. This may come from a relatively minor N_2 adsorption in zeolite-13X.

No correlation is observed between S and Q_{st} values for cases 1 and 2. For case 2, this might be anticipated; the S value depends on both ΔN_1 and α_{12}^{ads} values, but neither the ΔN_1 nor α_{12}^{ads} values show any correlation with Q_{st} values for case 2. For cases 3 and 4, the two VSA processes, positive correlations between S and Q_{st} values are observed as shown in Figure 6. However, the graphs provide some indication that very high Q_{st} values may not be desirable. There are not many data points above 50 kJ mol^{-1}, but the limited data with high Q_{st} values exhibit low values of S. From this limited data, we can speculate that a Q_{st} value around 50 kJ mol^{-1} may be optimal for obtaining high S values in cases 3 and 4.

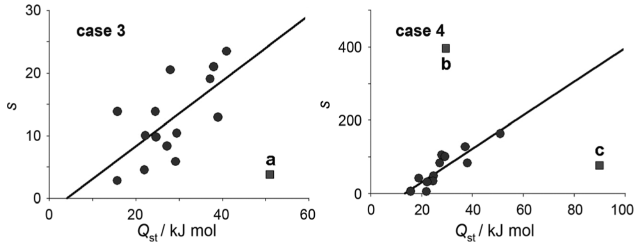

Figure 6. Relationship between sorbent selection parameter (S) and Q_{st} value for cases 3 and 4. The materials represented by a, b, and c are not included in the linear regression lines (solid lines): a) zeolite-5A; b) ZIF-78; c) ethylenediamine-$H_3[(Cu_4Cl)_3-(BTTri)_8]$. No correlations are observed for cases 1 and 2 (see Figure S6 in the Supporting Information).

5. Summary and Outlook

Metal-organic frameworks (MOFs) are one of the most exciting areas in current materials sciences, and the development of MOFs for CO_2 separation processes is particularly important for energy and environmental applications. Herein, we attempted to bridge between materials chemists, who are developing new materials, and chemical engineers, who are developing adsorption separation processes such as PSA and VSA. In particular, we discussed several criteria for quickly evaluating new materials for their potential in adsorption separation processes. These adsorbent evaluation criteria can be easily calculated from single-component isotherms at appropriate temperature and pressure ranges and may be useful for materials chemists as a way to quickly evaluate new materials for CO_2 separation processes. None of the criteria are perfect, and they are best considered together. The journey to commercializing a new separation technology is long and cannot be predicted based on these simple criteria alone.

Using the five adsorbent evaluation criteria, we reviewed the literature to identify the most promising MOFs and POPs for four important CO_2 separation processes using PSA and VSA processes. Comparisons with three commercially available adsorbents including zeolites showed that several MOFs are promising for CO_2 separation processes. From the assembled data, we found several interesting correlations between the heat of adsorption of CO_2 and the adsorbent evaluation criteria but no correlations with purely structural properties such as the pore size or surface area. These findings should be helpful for the design of better materials for CO_2 separation.

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