AIChE

Large-Scale Computational Screening of Metal-Organic Frameworks for CH_4/H_2 Separation

Dong Wu and Cuicui Wang
State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

Bei Liu
State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

Dahuan Liu, Qingyuan Yang, and Chongli Zhong
State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

DOI 10.1002/aic.12744

Molecular simulations were performed to study a diverse collection of 105 metal-organic frameworks (MOFs) for their ability to remove CH_4 from CH_4/H_2 mixture. To investigate the practical industrial application in a pressure swing adsorption (PSA) process, working capacity was also considered in addition to selectivity. The results show that MOFs are promising candidate for this separation, which give higher adsorption selectivity with similar working capacity and higher working capacity with similar selectivity than the traditional nanoporous materials such as carbonaceous materials and zeolites. To quantitatively describe the structure–property relationship for CH_4/H_2 mixture separation in MOFs, a new concept named "adsorbility" was defined, which shows strong correlation with limiting selectivity, with a correlation coefficient (r^2) of 0.86. This work shows that although MOFs are promising materials for CH_4/H_2 mixture separation, more investigations that consider both selectivity and working capacity are necessary to screen MOFs in practical PSA application. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 2078–2084, 2012

Keywords: metal-organic framework, molecular simulation, separation, selectivity, working capacity

Introduction

Hydrogen, regarded as a renewable and ecologically clean energy source, is increasing demanded in various fields including fuel cells, semiconductor processing, and petrochemical industry. To produce hydrogen, steam reforming is one of the widely used technologies.[1] In this process, it is very important to remove other impurities, such as methane, and adsorption separation, which is generally considered to be low in energy consumption, is an attractive technology to handle this. In the past decades, a variety of nanoporous materials, such as carbonaceous materials and zeolites, have been investigated for the adsorptive separation of CH_4/H_2,[2–5] but the reported selectivities are not sufficiently high for practical applications up to now. Therefore, significant research efforts are being paid toward designing new materials for the separation of this binary mixture.

Recently, metal-organic frameworks (MOFs) are receiving increasing attention,[6–9] which have shown potential applications in many fields, such as gas storage,[10,11] catalysis,[12–14] and separation.[15,16] Particularly, a series of MOFs have been explored for CH_4/H_2 separation, which exhibit higher selective adsorption capability compared with traditional porous materials,[2–5,17] indicating this kind of materials to be the most attractive candidate for CH_4/H_2 adsorptive separation. To date, thousands of MOFs have been synthesized, and this number is nearly infinite due to the large variety of possible metal corner units and organic linkers.[18] They are much richer in the variety of chemical composition, pore size, and topology. Therefore, the structure–property relationships for MOFs are not very clear, hampering the development of new MOFs for this specific application. In this aspect, a purely experimental method for designing optimal MOFs is inefficient at best, for which molecular simulation provides a useful complement or alternative. Compared with experiment, molecular simulation is most convenient in isolating influencing factors to quantify their separate contributions to the behaviors of MOFs, as well as the cooperative effects of a set of selected factors; this information is very important in understanding the relationships between structure and property. On the other hand, molecular simulation is also an efficient way for large-scale screening of MOFs for a targeted application.

Although several computational studies have been performed on the adsorptive separation of CH_4/H_2 in

---

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to D. Liu at liudh@mail.buct.edu.cn, and C. Zhong at zhongcl@mail.buct.edu.cn, and B. Liu at liub@cup.edu.cn.

MOFs,[19–21] the MOFs considered in one study is small and usually limited to the well-known species. Therefore, in this work a large-scale computational screening study was performed on a diverse collection of 105 MOFs for their adsorptive separation performance on CH_4/H_2; the information obtained based on such a large database will allow us to find out the structure–property relationship for CH_4/H_2 adsorptive separation in MOFs, as well as to identify the key influencing factor. On the other hand, in the practical operation of the pressure swing adsorption (PSA) technology, working capacity is an important factor in addition to the adsorption selectivity, the working capacity for the MOFs with high selectivities screened was also studied. One goal of this work is to try to screen MOFs for practical applications by considering both adsorption selectivity and working capacity for CH_4/H_2 separation.

Model and Computational Details

MOF structures

In this work, 105 MOFs were considered with large diversity in chemistry and structure, including IRMOFs, Cu-BTC, PCNs, MILs, ZIFs, and some newly synthesized MOFs. The guest-free framework structures were constructed from their corresponding experimental single-crystal X-ray diffraction data using Materials Studio Visualizer.[22] The names of the MOFs and their structural properties are shown in Table S1 in the Supporting Information.

Force fields

CH_4 was modeled as a single Lennard–Jones (LJ) interaction site, and the potential parameters were taken from TraPPE force field, which was able to reproduce the critical parameters and liquid densities of alkanes.[23] The H_2 molecule was modeled as a two-site LJ molecule with the parameters obtained in our previous work by fitting the experimental PVT curve of bulk H_2 and validated with H_2 adsorption in IRMOFs.[24] For the MOFs, the Dreiding force field was adopted to calculate the interactions between adsorbates and frameworks.[25] The parameters were taken from the UFF force field for the metals that are not tabulated for the Dreiding force field.[26] All the LJ cross interaction parameters were determined by the Lorentz–Berthelot mixing rules. The above set of potential models has been successfully used to describe the adsorption,[24,27,28] separation,[29,30] and diffusion[24,31] of CH_4 and H_2 in MOFs. The potential parameters are listed in Table S2 in the Supporting Information.

Simulation details

Grand canonical Monte Carlo (GCMC) simulations were used to calculate the adsorption of CH_4/H_2 mixtures in the MOFs at 298 K. Similar to previous works,[24,27,30,32] all the MOFs were treated as rigid frameworks with atoms frozen at their crystallographic positions, because the effects of the dynamics of MOFs become significant only when the guests are large and/or strong guest–host interactions exist in the system at room temperature. The numbers of the unit cells contained in the simulation box are MOF-dependent, ranging from $1 \times 1 \times 1$ to $7 \times 7 \times 7$ so that enough molecules are accommodated to guarantee the simulation accuracy. Periodic boundary conditions have been applied in all three dimensions. A cutoff radius was set to 1.28 nm for the LJ interactions. For each state point, the number of steps in GCMC simulation was 2.0×10^7, where the first 10^7 steps were used for equilibration and the subsequent 10^7 steps for sampling the desired thermodynamics properties. A detailed description of the simulation methods can be found in Ref. 33.

The isosteric heat of adsorption Q_{st} was calculated from[34]

$$Q_{st} = RT - \frac{\langle U_{ff}N\rangle - \langle U_{ff}\rangle\langle N\rangle}{\langle N^2\rangle - \langle N\rangle\langle N\rangle} - \frac{\langle U_{sf}N\rangle - \langle U_{sf}\rangle\langle N\rangle}{\langle N^2\rangle - \langle N\rangle\langle N\rangle}, \quad (1)$$

where R is the gas constant, N is the number of molecules adsorbed, and $\langle\rangle$ indicates the ensemble average. The first and second terms are the contributions from the molecular thermal energy and adsorbate–adsorbate interaction energy U_{ff}, respectively. The third term is the contribution from the adsorbent–adsorbate interaction energy, U_{sf}. It should be noted that this form of the equation is only true if the gas phase behaves ideally.

In separation processes, a good measure of the ability for separation is the selectivity of a porous material for different components in mixtures. The selectivity for component A relative to component B is defined by $S = (x_A/x_B)(y_B/y_A)$, where x and y are the mole fractions of two components in the adsorbed and bulk phases, respectively.

Results and Discussions

Selectivity of CH_4/H_2 mixture in MOFs

In this work, 105 MOF materials were collected from literature, covering the most well-known subfamilies and some newly synthesized ones. We expect a systematic computational study based on such a large MOF database can give further insight into structure–property relationships for MOFs and general conclusions can be derived. Also, such a systematic study may lead to new findings. The equimolar CH_4/H_2 mixture was considered in this work for the convenience of comparing with existing works, and all the simulations were performed at 298 K.

The adsorption selectivities for CH_4 from the equimolar CH_4/H_2 mixture are shown in Figure 1, as a function of the bulk pressure up to 4.0 MPa. In all the MOFs, CH_4 is more preferentially adsorbed than H_2 due to the stronger dispersion interactions with the framework, and CUK-2, PCN-13, MOF-114, and MIL-102 show obvious higher selectivity than other MOFs. Generally speaking, there are two different trends in the pressure dependence of selectivity: one is the selectivity decreases monotonously with increasing pressure up to 4.0 MPa, and the other is that it is nearly pressure-independent or slightly increases with increasing pressure at low-pressure region, followed by a nearly pressure-independent or a slight decrease step at high pressures. The first trend of the pressure dependence behavior of selectivity can be attributed to the existence of different types of pores with small sizes in those MOFs, leading to strong confinement effects, and thus the packing effects start to work at low pressures, that is, the existence of small pores together with the heterogeneity in pore size results in a decrease of methane selectivity with increasing pressure in the pressure range studied. For example, there are two kinds of pores in ZIF-81 (0.39/0.74 nm) and four kinds of pores in IRMOF-9 (0.45/0.63/0.81/1.07 nm), respectively. In addition, the difference in the degree of confinement effect may induce that for some of the MOFs, the selectivity decreases rapidly with pressure (e.g., MOP-14), whereas for others, the decrease is much slower (e.g., IRMOF-9). On the other hand, in the

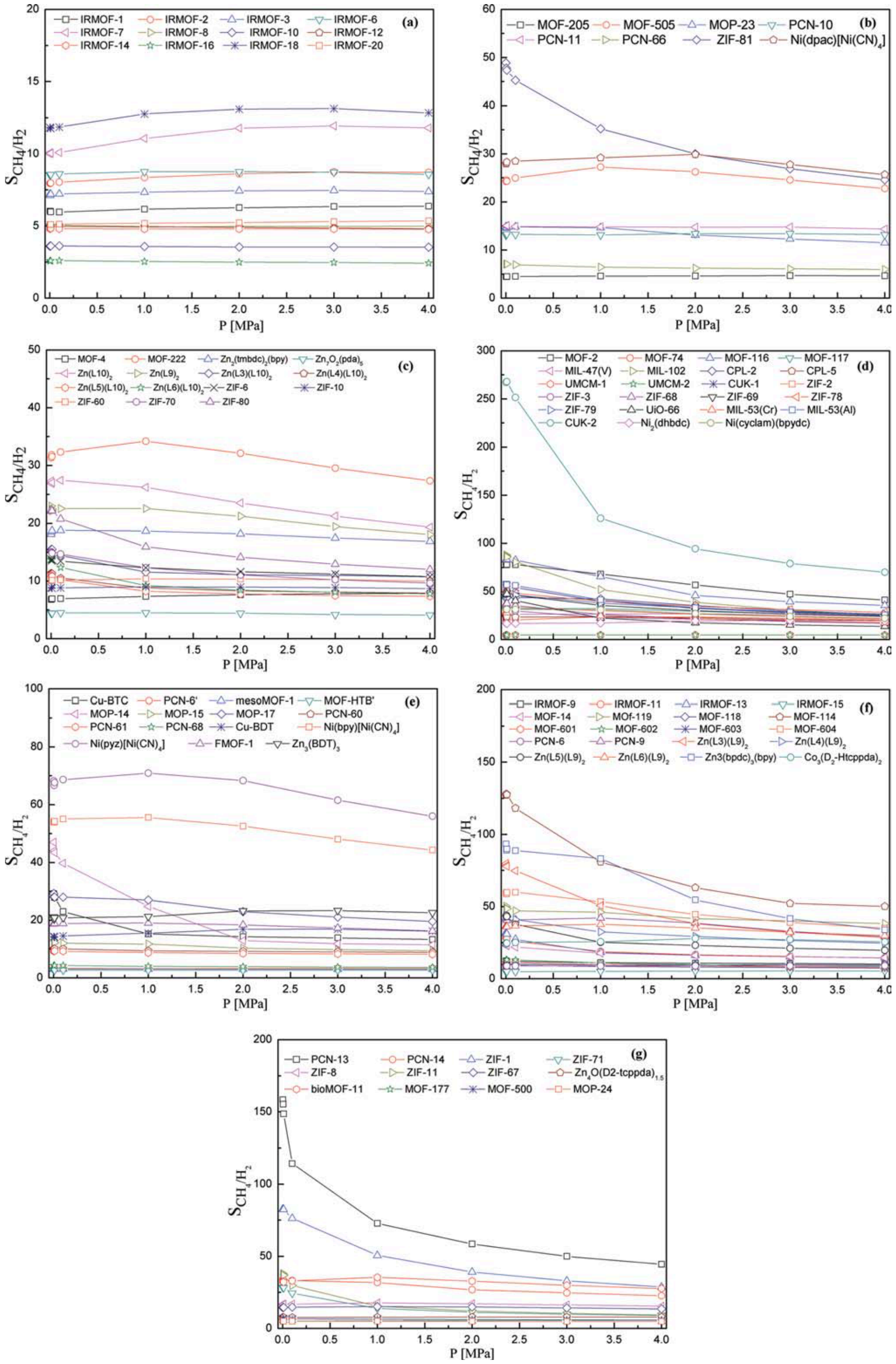

Figure 1. Selectivity for CH_4 in the equimolar CH_4/H_2 mixture at 298 K. Dots are connected by straight lines to guide the eye.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other MOFs showing the second trend, there is enough space in the pores of MOFs at low pressure, making the packing effect that favors hydrogen adsorption insignificant, leading to a nearly pressure-independent or slight increase of methane selectivity with increasing pressure. Among these MOFs, the packing effect becomes evident at moderate pressure in the materials with relative small pores, such as MOF-222, and the selectivity goes through a maximum followed by a slight decrease with further increasing pressure.

Separation of CH_4 from CH_4/H_2 mixture has also been performed in other porous materials, for example, at 303 K, the selectivity of CH_4 is 58.3 in Coconut carbon, 37.9 in 5A zeolite, 34.1 in Coal carbon, and 13.0 in Activated alumina[17]; all the above selectivites are the limiting selectivities estimated from the Henry's law constants (initial isotherm

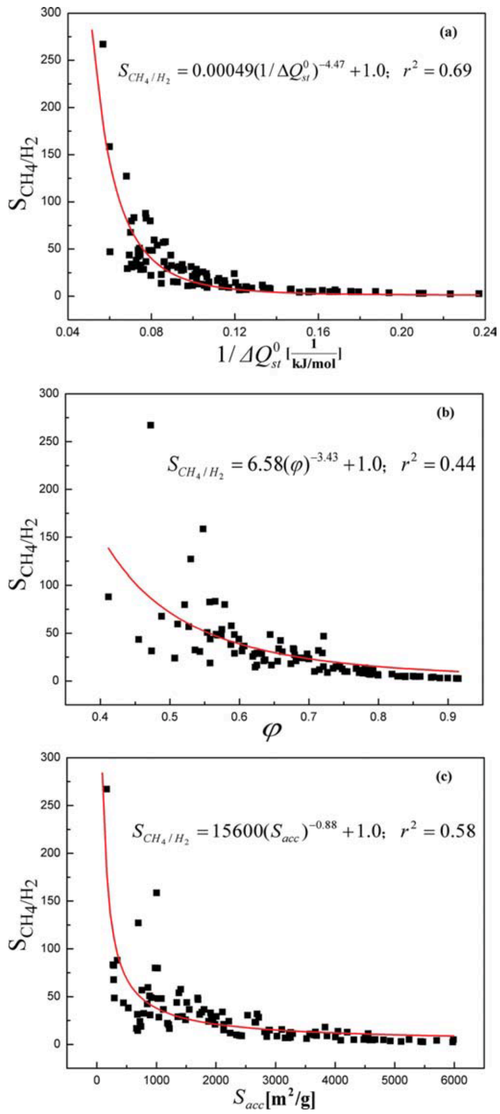

Figure 2. Limiting selectivity for CH_4 in the equimolar CH_4/H_2 mixture vs. the difference of isosteric heats of adsorption, porosity (ϕ) and specific accessible surface area (S_{acc}).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

slope) for CH_4 and H_2 adsorption. Obviously, Figure 1 demonstrates that several MOFs studied in this work, including CUK-2, PCN-13, MOF-114, and MIL-102, show much higher selectivity than these traditional materials, indicating that MOFs may be the most attractive candidate for CH_4/H_2 adsorptive separation.

Correlation with commonly used properties

To quantitatively understand the structure-selectivity relationships for MOFs, we have tried to correlate the selectivity of CH_4/H_2 mixture in the 105 MOFs at 0.001 MPa (mimic the infinite dilution), which is the limiting selectivity of a MOF, reflecting the intrinsic separation capability of the material. The correlations between the limiting selectivity and the difference of isosteric heats of adsorption of the two components are shown in Figure 2. Furthermore, correlations with porosity (ϕ) and specific accessible surface area (S_{acc}) were also tried. The results are also shown in Figure 2. Obviously, no good correlation is found.

The correlation between selectivity and pore size was not tried, because some MOFs have either more than one kind of pores with different sizes, as shown in Supporting Information Table S1. Based on the above calculations, this work might come to a conclusion that the selectivity of MOFs does not show good correlations with the commonly used single property, such as the difference of isosteric heats of adsorption of the two components, porosity, and specific accessible surface area, which should be the interplay of various properties.

There are quite limited experimental works on the correlation of selectivity with property. The only one we know is the work of Banerjee et al.[35] Their experimental observations show that even for MOFs with similar pore shape and topology, such as ZIFs, there is no good correlation between selectivity and the structure of MOFs, such as specific surface area. These agree with the general conclusions obtained in this work.

Development of a new concept to characterize MOFs

The above correlations show that the selectivity of MOFs for a given mixture is affected by the interplay of various factors and cannot correlate strongly with the available single property. As the various influencing factors may have conflict contributions to selectivity, making the structure–selectivity relationships for MOFs are not well-understood to date, and the design of MOFs for the separation of a given system based, to large extent, on a trial-and-error procedure. On the other hand, if a single parameter is developed that can characterize the main feature of a gas/MOF system, quantitative structure–property relationships models may be established for MOFs, contributing to the further understanding of structure–

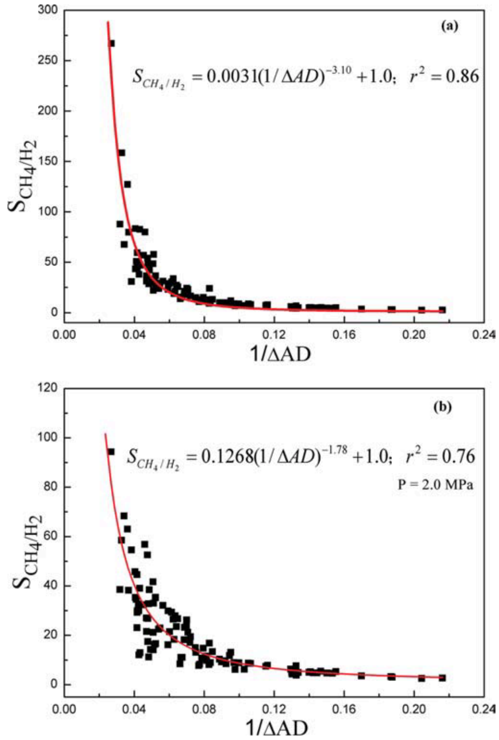

Figure 3. Limiting selectivity (a) and selectivity at 2.0 MPa (b) vs. 1/ΔAD from the equimolar mixture CH_4/H_2.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. The Simulated Selectivities at Different Pressures for the 10 Selected MOFs with Highest Limiting Selectivities for the Equimolar CH_4/H_2 at 298 K

MOF	Limiting selectivity	0.1 MPa	1.0 MPa	2.0 MPa	3.0 MPa	4.0 MPa
CUK-2	267.10	251.53	126.07	94.33	79.06	69.82
PCN-13	158.50	114.21	72.75	58.49	50.02	44.45
MOF-114	127.21	118.19	80.90	63.06	52.21	50.12
MIL-102	87.89	80.57	51.80	38.56	30.62	25.39
MOF-116	83.32	82.58	65.54	45.75	39.19	35.51
ZIF-1	82.68	76.23	50.60	39.03	33.00	28.79
MOF-2	79.96	77.83	68.00	56.81	47.20	41.12
$Zn(L3)(L9)_2$	79.78	74.76	50.63	38.21	32.33	28.51
$Ni(pyz)[Ni(CN)_4]$	67.63	70.89	68.35	61.50	56.01	52.25
MOF-604	59.53	59.93	53.29	44.59	38.92	34.99

selectivity relationships for MOFs, as well as future design of MOFs with tailored separation performance.

In solution theory, solubility parameter δ (also denoted by *SP*) plays an important role,[36] which can be used as an estimate of the compatibility of two components in solution. Can we develop a similar concept named "adsorbility" (AD) to describe the "compatibility" of the two components adsorbed in a MOF? The "compatibility" here should be identical to "selectivity."

Solubility parameter is defined as the square root of cohesive energy density ($E_{coh} = H^{vap}/v^L$), the energy of vaporization per unit liquid volume. Therefore, we propose a similar concept for nanoporous materials defined as:

$$E_{ad} = \frac{Q_{st}^0}{\varphi} \tag{2}$$

where Q_{st}^0 is the isosteric heat of adsorption at infinite dilution in kJ/mol for an adsorbate, and ϕ is the free volume per unit volume of the material in cm^3/cm^3, also known as porosity. Therefore, E_{ad} is the adsorption energy density based on specific free volume, having a similar physical meaning to cohesive energy density. In this work, instead of defining the AD as the square root of E_{ad}, we make them identical (AD $= E_{ad}$) so that the physical meaning of parameter AD is more clear, that is, a measure of adsorption energy density for a gas in a given nanoporous material.

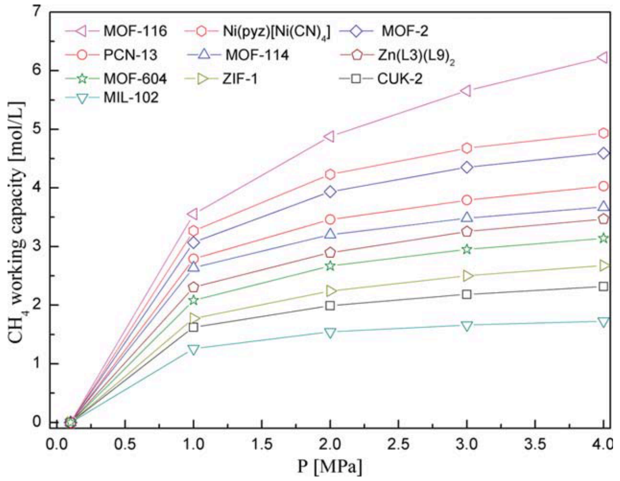

Figure 4. CH_4 working capacities for the ten selected MOFs with highest limiting selectivities at 298 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the concept of AD is similar to solubility parameter, it is expected the new parameter can also serve as a measure of the "compatibility" of the two gases adsorbed in a nanoporous material, and thus the difference in AD (ΔAD) of the components can be used to characterize the selectivity. It should be pointed out that the new concept is general for any nanoporous materials, while in this work, we will apply it to MOFs.

Correlation between selectivity and AD

The limiting selectivities of CH_4 from the CH_4/H_2 mixture as a function of 1/ΔAD of the two components are shown in Figure 3a. A comparison with the correlations in Figure 2 shows that limiting selectivity correlates much better with AD, indicating that AD can grasp the main feature of a gas/MOF system, approximately representing the interplay of various influencing factors. Furthermore, the selectivity at 2.0 MPa, representing higher pressure, was further correlated with ΔAD as shown in Figure 3b. It can be seen that good correlation still hold, although a little worse than that of limiting selectivity; this means ΔAD may also be useful in correlating selectivity at high pressures.

From the above discussion, synthesizing MOFs with large ΔAD can serve as a general design criterion for the development of MOFs as well as for preliminary screening MOFs for separation applications. In order to obtain large ΔAD, the differences in the interactions between the two adsorbates and the MOF should be as large as possible, and the MOF should have small porosity. For example, in CUK-2, the difference of the interactions between the adsorbates (CH_4 and H_2) and material is large with smaller porosity than most MOFs considered in this work. Thus, it shows high selectivities over the whole pressure range. However, the interaction between adsorbate and MOFs is determined by the interplay of several MOF structural properties, such as surface area, pore volume, chemical composition, topology and so on, and the relationship between them is not very clear at the moment that deserves further study.

Further screening of MOFs based on working capacity

In the PSA process, working capacity, defined as the difference between the capacity at the high intake pressure and at the lower purge pressure, is an important factor to evaluate the efficiency of the process,[37–39] and an ideal adsorbent should have both high adsorption selectivity and working capacity.[40] Therefore, we further calculated the working capacities of CH_4 in the CH_4/H_2 mixture for the 10 MOFs showing highest limiting selectivity (Table 1) assuming a purge pressure of 0.1 MPa. The pressure dependence of the working capacities is shown in Figure 4.

Table 2. Comparison of the Limiting Selectivity and CH_4 Working Capacity between 0.3 and 0.05 MPa for Equimolar CH_4/H_2 Mixture for the Selected MOFs and Some Traditional Materials

MOFs*	MOF-604	CPL-2	ZIF-11	PCN-14	ZIF-67	PCN-10
Limiting selectivity	59.53	43.5	38.09	33.92	14.5	13.08
CH_4 working capacity (mol/L)	1.175	0.600	0.572	1.379	0.508	0.727
Traditional Materials†	Coconut carbon	5A zeolite	Coal carbon	Silica gel	Activated alumina	
Limiting selectivity	58.3	37.9	34.1	14.3	13.0	
CH_4 working capacity (mol/L)	0.670	0.580	0.600	0.200	0.120	

*Simulated results obtained in this work.
†Experimental results obtained in Ref. [17].

The results in Figure 4 show that the two efficiency factors may have conflict for a given MOF, that is, a MOF with high selectivity may show small working capacity; this is particularly clear if we consider CUK-2 with highest limiting selectivity as well as selectivities at various pressures among the 10 MOFs shown in Table 1; however, it shows nearly lowest working capacity at various working pressures. Therefore, evaluations based solely on adsorption selectivity are not enough to assess properly a PSA process, and a reasonable evaluation must also consider the working capacity. However, in the previous studies, only adsorption selectivity was considered. Therefore, further studies taking into account the two influencing factors are needed for practical applications.

The CH_4 working capacity between 0.3 and 0.05 MPa at 303 K were investigated in some traditional porous materials, such as Coconut carbon, Coal carbon, 5A zeolite, Silica gel, and Activated alumina,[17] as shown in Table 2. To make a comparison, the CH_4 working capacities between 0.3 and 0.05 MPa in MOFs were also calculated, and the results are listed in Table 2, taking CPL-2, MOF-604, ZIF-11, PCN-14, ZIF-67, and PCN-10 as examples. Obviously, the MOFs exhibit higher limiting selectivity on the condition of similar working capacity (such as, CPL-2 and 5A zeolite), while higher working capacity with similar limiting selectivity (such as, PCN-14 and Coal carbon). It should be noted that the limiting selectivity and working capacities at different pressures was chosen to make a comparison because only this set of experimental results for traditional materials can be found in literature as far as we know.[17] To make a more reasonable comparison, the selectivity at the pressure working capacity was calculated was given in Table 3, where the values for the traditional materials were taken from the literature.[41] Similar conclusion can be obtained. These results further indicate that MOFs are promising materials for CH_4/H_2 separation using PSA process compared to other porous adsorbents.

Table 3. Comparison of the Simulated Selectivity at 2.0 MPa and Corresponding CH_4 Working Capacity between 2.0 and 0.1 MPa for Equimolar CH_4/H_2 Mixture for the Selected MOFs and Some Traditional Materials[41]

MOFs	MOF-604	MIL-102	IRMOF-20	IRMOF-8
Selectivity (2.0 MPa)	44.59	38.56	5.23	4.97
CH_4 working capacity (mol/L)	2.67	1.54	2.02	1.84
Traditional materials	ITQ-29	CHA	TSC	
Selectivity (2.0 MPa)	7.60	9.49	4.93	
CH_4 working capacity (mol/L)	2.60	2.32	1.57	

Conclusions

The large-scale computational study based on a diverse collection of 105 MOFs shows that MOFs are promising candidates for CH_4/H_2 mixture separation, which give higher adsorption selectivity with similar working capacity and higher working capacity with similar selectivity than the traditional adsorbents such as carbonaceous materials and zeolites. The new parameter, AD, defined in this work shows strong correlation with the limiting selectivity of CH_4/H_2 mixture in the 105 MOFs considered. The results on the working capacities for the 10 MOFs with highest limiting selectivity illustrate that the two efficiency factors that describe a real PSA process may have conflict, and a proper assessment of a PSA process should consider the both factors. This work shows that although MOFs are promising candidates for CH_4/H_2 mixture separation, more investigations that consider the real operating conditions applied in a PSA process should be performed.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos.: 20725622, 20821004, 20906002, 21006126). B. L. thanks the Research Funds of China University of Petroleum, Beijing (BJBJRC-2010-01).

Literature Cited

1. Hufton JR, Mayorga S, Sircar S. Sorption-enhanced reaction process for hydrogen production. *AIChE J.* 1999;45:248–256.
2. Mitchell MC, Gallo M, Nenoff TM. Computer simulations of adsorption and diffusion for binary mixtures of methane and hydrogen in titanosilicates. *J Chem Phys.* 2004;121:1910–1916.
3. Poshusta JC, Tuan VA, Pape EA, Noble RD, Falconer JL. Separation of light gas mixtures using SAPO-34 membranes. *AIChE J.* 2000;46:779–789.
4. Morales-Cas AM, Moya C, Coto B, Vega LF, Calleja G. Adsorption of hydrogen and methane mixtures on carbon cylindrical cavities. *J Phys Chem C.* 2007;111:6473–6480.
5. Chen HB, Sholl DS. Predictions of selectivity and flux for CH4/H2 separations using single walled carbon nanotubes as membranes. *J Membr Sci.* 2006;269:152–160.
6. Kitagawa S, Kitaura R, Noro S. Functional porous coordination polymers. *Angew Chem Int Ed Engl.* 2004;43:2334–2375.
7. Liu DH, Zhong CL. Understanding gas separation in metal-organic frameworks using computer modeling. *J Mater Chem.* 2010;20:10308–10318.
8. Férey G, Serre C. Large breathing effects in three-dimensional porous hybrid matter: facts, analyses, rules and consequences. *Chem Soc Rev.* 2009;38:1380–1399.
9. Long JR, Yaghi OM. The pervasive chemistry of metal-organic frameworks. *Chem Soc Rev.* 2009;38:1213–1214.
10. Murray LJ, Dinca M, Long JR. Hydrogen storage in metal-organic frameworks. *Chem Soc Rev.* 2009;38:1294–1314.
11. Han SS, Mendoza-Cortes JL, Goddard WA, III. Recent advances on simulation and theory of hydrogen storage in metal-organic frameworks and covalent organic frameworks. *Chem Soc Rev.* 2009;38:1460–1476.

12. Ma LQ, Abney C, Lin WB. Enantioselective catalysis with homochiral metal-organic frameworks. *Chem Soc Rev.* 2009;38:1248–1256.
13. Lee JY, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT. Metal-organic framework materials as catalysts. *Chem Soc Rev.* 2009;38:1450–1459.
14. Farrusseng D, Aguado S, Pinel C. Metal-organic frameworks: opportunities for catalysis. *Angew Chem Int Ed Engl.* 2009;48: 7502–7513.
15. Li JR, Kuppler RJ, Zhou HC. Selective gas adsorption and separation in metal-organic frameworks. *Chem Soc Rev.* 2009;38:1477–1504.
16. Czaja AU, Trukhan N, Müller U. Industrial applications of metal-organic frameworks. *Chem Soc Rev.* 2009;38:1284–1293.
17. Ludwig K. Development of new pressure swing adsorption technology to recover high valued products from chemical plant refinery waste streams. Report to DOE, DE-FC36-00CH11022, 2004.
18. Düren T, Bae YS, Snurr RQ. Using molecular simulation to characterise metal-organic frameworks for adsorption applications. *Chem Soc Rev.* 2009;38:1237–1247.
19. Yang QY, Zhong CL. Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks. *J Phys Chem B.* 2006;110:17776–17783.
20. Liu B, Yang QY, Xue CY, Zhong CL, Chen BH, Smit B. Enhanced adsorption selectivity of hydrogen/methane mixtures in metal-organic frameworks with interpenetration: a molecular simulation study. *J Phys Chem C.* 2008;112:9854–9860.
21. Guo HC, Shi F, Ma ZF, Liu XQ. Molecular simulation for adsorption and separation of CH4/H2 in zeolitic imidazolate frameworks. *J Phys Chem C.* 2010;114:12158–12165.
22. *Accelrys, Inc. Materials Studio, 3.0 V.* Accelrys Inc: San Diego, CA, 2003.
23. Martin MG, Siepmann JI. Transferable potentials for phase equilibria. I. united-atom description of n-alkanes. *J Phys Chem B.* 1998;102:2569–2577.
24. Yang QY, Zhong CL. Molecular simulation of adsorption and diffusion of hydrogen in metal-organic frameworks. *J Phys Chem B.* 2005;109:11862–11864.
25. Mayo SL, Olafson BD, Goddard WA,III. Dreiding: a generic force field for molecular simulations. *J Phys Chem.* 1990;94:8897–8909.
26. Rappé AK, Casewit CJ, Colwell KS, Goddard WA III, Skiff WM. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J Am Chem Soc.* 1992;114:10024–10035.
27. Düren T, Sarkisov L, Yaghi QM, Snurr RQ. Design of new materials for methane storage. *Langmuir.* 2004;20:2683–2689.
28. Garberoglio G, Skoulidas AI, Johnson JK. Adsorption of gases in metal organic materials: comparison of simulations and experiments. *J Phys Chem B.* 2005;109:13094–13103.
29. Yang QY, Zhong CL. Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks. *J Phys Chem B.* 2006;110:17776–17783.
30. Liu B, Yang QY, Xue CY, Zhong CL, Chen BH, Smit B. Enhanced adsorption selectivity of hydrogen/methane mixtures in metal-organic frameworks with interpenetration: a molecular simulation study. *J Phys Chem C.* 2008;112:9854–9860.
31. Xue CY, Zhou Z, Liu B, Yang QY, Zhong CL. Methane diffusion mechanism in catenated metal-organic frameworks. *Mol Simul.* 2009;35:373–380.
32. Liu DH, Yang QY, Zhong CL. Adsorption of methane in heterometallic metal-organic frameworks with anions: a molecular simulation study. *Mol Simul.* 2009;35:213–219.
33. Frenkel D, Smit B. *Understanding Molecular Simulation: From Algorithms to Applications*. San Diego: Academic Press, 2002.
34. Do DD, Do HD. Modeling of adsorption on nongraphitized carbon surface: GCMC simulation studies and comparison with experimental data. *J Phy Chem B.* 2006;110:17531–17538.
35. Banerjee R, Furukawa H, Britt D, Knobler C, O'Keeffe M, Yaghi OM. Control of pore size and functionality in isoreticular zeolitic imidazolate frameworks and their carbon dioxide selective capture properties. *J Am Chem Soc.* 2009;131:3875–3877.
36. Barton AF. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*. Boca Raton, Florida: CRC Press, 1983.
37. Yang S, Choi DY, Jang SC, Kim SH, Choi DK. Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas. *Adsorption.* 2008;14:583–590.
38. Wells BA, Chaffee AL. Modeling gas separation in metal-organic frameworks. *Adsorption.* 2011;17:255–264.
39. Hamon L, Jolimaître E, Pirngruber GD. CO2 and CH4 separation by adsorption using Cu-BTC metal-organic framework. *Ind Eng Chem Res.* 2010;49:7497–7503.
40. Sircar S, Golden TC. *Pressure swing adsorption technology for hydrogen production*. In:Liu K,Song C,Subramani V, editors. *Hydrogen and Syngas Production and Purification Technologies*. Hoboken, NJ: Wiley-AIChE, 2010:414–450.
41. Krishna R, van Baten JM. In silico screening of metal-organic frameworks in separation applications. *Phys Chem Chem Phys.* 2011;13:10593–10616.

Manuscript received April 14, 2011, and revision received Jun. 13, 2011.