Identifying Highly Selective Metal Organic Frameworks for CH₄/H₂ Separations Using Computational Tools

Yasemin Basdogan,[†] Kutay Berk Sezginel,[†] and Seda Keskin*

Department of Chemical and Biological Engineering, Koc University, Rumelifeneri Yolu, Sariyer, 34450, Istanbul, Turkey

Supporting Information

ABSTRACT: The large number of metal organic frameworks (MOFs) represents both an opportunity and a challenge for identification of materials exhibiting promising properties in gas separations. We used molecular simulations to screen 250 different MOF structures in order to examine their adsorption-based CH₄/H₂ separation performances. Adsorption selectivity, working capacity, sorbent selection parameter, and regenerability of MOFs were calculated and compared with those of traditional nanoporous materials. The accuracy of simple models that can predict adsorption selectivity of MOFs based on structural properties of materials was discussed. With the use of molecular dynamics, gas diffusivities were computed in the MOFs which were identified as the top performing materials for adsorption-based CH₄/H₂ separation. Membrane selectivities of these MOFs were predicted to discuss kinetic separation performances of materials. Results showed that there is a significant number of MOFs that exhibit extraordinarily large adsorption-based and membrane-based CH₄/H₂ selectivities compared to well-known nanoporous materials such as zeolites. Using MOFs as adsorbents rather than membranes would be more efficient in CH₄/H₂ separation.

1. INTRODUCTION

Hydrogen is considered as a renewable and clean energy source for several applications such as fuel cells, semiconductor processing, and the petrochemical industry. Hydrogen purification from various process streams constitutes the largest commercial use of pressure swing adsorption (PSA) technology.¹ Steam reforming of CH₄ is the most widely used technology to produce pure hydrogen. The removal of impurities such as CH₄ and other hydrocarbons is crucial in this process. Separation of CH₄ from H₂ is specifically important in refineries. The gas mixture is generally 50% H₂ at 5–10 bar, and the impurities are C1–C5 hydrocarbons. Among the hydrocarbons, CH₄ represents the smallest of the impurities. The van der Waals forces between CH₄ and the surface of a porous material is the weakest.² Therefore, CH₄/H₂ separation is considered as the most difficult separation to achieve in refinery off-gas separation processes. Several different nanoporous materials, such as carbonaceous materials and zeolites, have been investigated for the adsorption-based separation of CH₄/H₂ mixture. The molecular simulation study of Chen and Sholl³ showed that defect-free single walled carbon nanotubes exhibit a CH₄/H₂ selectivity of 35 from an equimolar CH₄/H₂ mixture at low pressures and room temperature. Morales-Cas et al.⁴ studied cylindrical carbon cavities of different sizes using molecular simulations and showed that maximum CH₄ selectivity is around 13 at 10 bar. Mitchell et al.⁵ employed molecular dynamics simulations for an equimolar CH₄/H₂ mixture in three different titanosilicates, naturally occurring zorite, and two synthetic titanosilicates, ETS-4 and ETS-10. Their computed adsorption selectivities were generally less than 5 at 10 bar, 500 °C. These reported selectivities for carbon nanotubes and zeolites are not sufficiently high for practical applications suggesting that

identification of new nanoporous materials that can achieve CH₄/H₂ separation with high selectivity is required.

Metal organic frameworks (MOFs) have appeared as promising alternatives to well-known nanoporous materials in adsorption-based gas separations due to their high porosities, large surface areas, low densities, and good mechanical and chemical stabilities.^{6–8} MOFs are composed of organic linkers connected by metal cations, and theoretically unlimited number of structures can be synthesized by combining different metals and linkers. MOFs offer a large versatility in geometry and chemical property suggesting that it is possible to find an ideal MOF for a specific gas separation. Molecular simulations play an increasingly important role in understanding the potential of MOFs in gas separations. Grand Canonical Monte Carlo (GCMC) simulations are widely used to predict adsorption isotherms of various gases in MOFs. Selectivities calculated from simulated adsorption isotherms are generally found to be in good agreement with the experiments.⁹ Most of the GCMC studies in the literature focused on separation of CO₂/CH₄,^{10–14} whereas a limited number of studies examined the CH₄/H₂ separation potential of MOFs.

Yang and Zhong¹⁵ performed molecular simulations for the adsorption-based separation of CH₄/H₂ mixtures using MOF-5 and CuBTC. They reported CH₄ selectivity of 5 and 12 for MOF-5 and CuBTC, respectively, from an equimolar mixture of CH₄/H₂ at 10 bar, 298 K. Liu et al.¹⁶ computed adsorption selectivity of isorecticular MOFs (IRMOFs) IRMOF-9, -10, -11, -12, -13, and -14 for equimolar CH₄/H₂ mixtures and reported selectivities less than 25 at 10 bar, 298 K. They then showed

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that CH₄ selectivity is much enhanced in the mixed-ligand interpenetrated MOFs compared to their noninterpenetrated counterparts and reported selectivities around 50 at 10 bar and 298 K.¹⁷ Adsorption selectivity of Zn(bdc)(ted)_{0.5} was computed using GCMC simulations, and a selectivity of 50 was reported at 10 bar, 298 K.¹⁸ Keskin and Sholl¹⁹ calculated CH₄ selectivity of IRMOF-8, -9, -10, -14 and covalent organic framework (COF) COF-102 as ~5, 22, 5, 5, and 12, respectively, using GCMC simulations at 10 bar, 298 K. Guo et al.²⁰ employed GCMC simulations to study adsorption and separation characteristics of CH₄/H₂ in MOF-5 and five zeolitic imidazolate frameworks (ZIFs), including ZIF-3, -8, -10, -60, and -67. Their reported CH₄ selectivities were moderate, between 5 and 13, for these six MOFs at 10 bar and 298 K. Atci and Keskin²¹ studied the CH₄/H₂ separation performance of 15 different ZIFs and showed that several ZIFs exhibit higher selectivities than traditional zeolites CHA, ITQ-29, and LTA-Si, and CH₄ working capacities of ZIFs are similar to zeolites. COFs were also examined for this separation, and GCMC simulations showed that COF-6 outperforms traditional zeolites CHA, LTA, and ITQ-29 because of its higher CH₄ selectivity (20 at 10 bar, 298 K).²² Liu et al.²³ employed GCMC simulations to predict selectivity of MIL-101 (Materials of the Institute Lavoisier) series and showed that CH₄ selectivity of these materials varies between 6 and 10 at 10 bar for different bulk compositions of CH₄/H₂ mixtures. Peng et al.²⁴ showed that selectivity of CH₄/H₂ hardly changes with pressure, exhibiting a value of 4 for UCMC-1 (University of Michigan Crystalline Material) and 5 for UCMC-2.

As can be seen from this literature summary, most studies focused on either a single or a few MOFs at a time to examine the potential of MOFs in adsorption-based CH₄/H₂ separation. The type of MOFs was generally limited to well-known subgroups such as ZIFs, COFs, MILs, and maximum tens of materials were studied from the same material family. In this study, we used molecular simulations to assess adsorption-based CH₄/H₂ separation performance of a large number of MOFs. We studied 250 different MOFs and showed that adsorption-based separation performances of MOFs vary significantly when materials with a wide range of chemistry are considered. The first study in the literature on large-scale computational screening of MOFs for adsorption-based CH₄/H₂ separation was performed by Zhong's group²⁵ who examined CH₄/H₂ selectivity of 105 different MOFs using GCMC simulations. They reported adsorption selectivity of each MOF as a function of pressure (up to 40 bar) at room temperature and identified three MOFs that exhibit selectivity greater than 100 at limiting pressure (0.01 bar). However, adsorption-based separation performance of materials cannot be simply assessed by only considering selectivity. Three other parameters, working capacity, sorbent selection parameter, and regenerability are also very important to evaluate the efficiency of an adsorption-based separation process. In this work, we calculated these three parameters in addition to adsorption selectivity for each MOF. Selectivity and working capacity of MOFs were also compared with traditional adsorbents in order to assess the potential of MOFs in adsorption-based CH₄/H₂ separation.

We used molecular simulations to calculate both ideal selectivity and mixture selectivity as a function of adsorption pressure. To the best of our knowledge, no computational study has been done to compare ideal and mixture selectivity of a large number MOFs at a wide range of pressures for CH₄/H₂

separation. This comparison is important because experimental studies on MOFs generally measure single-component gas adsorption isotherms and report ideal selectivity of the material. The discrepancy between two selectivities was examined to discuss if intrinsic (ideal) selectivity of MOFs obtained from single-component gas adsorption isotherms can be used to get an initial estimate about adsorbent performance of materials.

Molecular simulations for mixtures can be time-consuming especially if the number of materials to be screened is high. Simple models that can predict selectivity of MOFs are very useful to efficiently and accurately screen materials for a specific separation application. Therefore, we used a simple model to predict adsorption selectivity of MOFs based on structural properties of materials such as pore volume and surface area. We compared predictions of our model with the direct results of GCMC simulations to discuss accuracy of our model. Two other models that were recently suggested in the literature to predict adsorption selectivity of nanoporous materials were also examined to understand which parameters are important in determining adsorption selectivity of MOFs.

Besides adsorption-based separation, membranes can be used to separate CH₄/H₂ mixtures based on kinetic properties of gases in the pores of MOFs. Predicting membrane properties of MOFs requires the computation of gas diffusivities in MOFs. Haldoupis et al.²⁶ calculated ideal H₂/CH₄ selectivity of MOF membranes within Henry's regime for 143 MOF structures using computational tools. They approximated diffusivity as the net activation energy for diffusion of the single-component gas molecules through MOFs. In this work, we examined membrane-based separation performance of MOFs that show high adsorption selectivity. We used direct molecular dynamics simulations to compute diffusion coefficients of gases in MOFs which were identified as the top performing materials for adsorption-based CH₄/H₂ separation. Diffusivity of each gas component was calculated at the corresponding adsorbed loadings in the binary mixture. In this way, we calculated mixture selectivity of the membrane which considers intermolecular interactions between different gas species.

2. COMPUTATIONAL DETAILS

2.1. MOFs. We considered 250 different MOFs in this work. The solvent-free MOF database constructed by Snurr et al.²⁷ was used in addition to 45 MOFs taken from our previous study²⁸ to cover well-known MOFs (such as MOF-5, CuBTC) and widely studied subfamilies (such as COFs and ZIFs). In this way, a representative structural database was obtained to span a wide range of chemical functionalities. The crystal structures of all MOFs were taken from the Cambridge Crystallographic Data Centre (CCDC).²⁹ The complete list of studied MOFs including the CCDC names and common names are given in Table S1 of the [Supporting Information](#) (SI). Pore volumes and surface areas of MOFs were computed using the algorithm of Sarkisov et al. (Poreblazer) and the method of Düren et al., respectively.^{30,31} We used the default force field, Universal Force Field (UFF)³² in the Poreblazer algorithm. The values of parameters such as sigma of the He atom, epsilon of the He atom, sigma of the N atom, and temperature were kept at their default values of 2.58 Å, 10.22 K, 3.314 Å and 298 K, respectively. The cutoff distance and cubelet size were used as 12.8 and 0.2 Å, respectively. The largest anticipated pore diameter was increased to 100 Å and the size of the bin was decreased to 0.1 Å. The method of Düren et al. was used to calculate gravimetric surface area.³¹

The diameters of the framework atoms were taken from UFF, and the diameter of the probe molecule was set to 3.681 Å.

2.2. Molecular Simulations. Grand Canonical Monte Carlo (GCMC) is a well-known method to compute the adsorption isotherm of gases in nanoporous materials.³³ Single-component and binary mixture GCMC simulations were performed to calculate adsorbed amounts of CH₄ and H₂ in MOFs. The adsorbed amounts of each gas component were calculated by specifying the bulk pressure, temperature, and composition of the bulk gas mixture in GCMC simulations. Four different types of moves were considered for single-component GCMC simulations including translation, rotation, insertion, and deletion of a molecule. In the binary mixture GCMC simulations, another trial move, the exchange of molecules was also performed. The Lorentz–Berthelot mixing rules were employed. The cutoff distance for truncation of the intermolecular interactions was set to 13 Å. Periodic boundary conditions were applied in all simulations. For GCMC simulations, a simulation box of 2 × 2 × 2 crystallographic unit cells was used. During the simulations, 1.5 × 10⁷ steps were performed to guarantee the equilibration and 1.5 × 10⁷ steps were performed to sample the desired properties. The isosteric heat of adsorption (Q_{st}), the difference in the partial molar enthalpy of adsorbate between the bulk and adsorbed phase, was calculated from the GCMC simulations as described in the literature.³⁴ The Q_{st} values of gases were calculated from the single-component GCMC simulations at their corresponding partial pressures in the binary mixtures.

In molecular simulations, single-site spherical Lennard-Jones (LJ) 12–6 potential was used to model H₂³⁵ and CH₄³⁶ molecules. UFF³² was used for 219 MOFs, the Dreiding³⁷ force field was used for 24 MOFs, and modified force fields were used for 7 MOFs. In cases where the potential parameters are not available in the Dreiding force field, these parameters were taken from the UFF. The force fields were selected based on the results of previous simulation studies^{28,38,39} that show a good agreement with the available experimental gas uptake data of MOFs. Detailed information about the force fields used for each MOF can be found in Table S1 of [Supporting Information](#).

We also performed Equilibrium Molecular Dynamics (EMD) simulations to compute self-diffusivities of CH₄/H₂ mixtures in the MOFs that are identified to exhibit high adsorption selectivity. The initial states of EMD simulations with the appropriate adsorbate loadings were obtained from the GCMC simulations, and each system was equilibrated for 20 ps prior to taking data. To use the membrane model given in the literature,¹⁹ we performed EMD simulations at the appropriate adsorbate loadings taken from GCMC simulations. The Nosé–Hoover thermostat was applied to run EMD simulations at NVT ensemble.³³ At least 20 independent EMD simulations with a length of 16 ns were performed to compute self-diffusivities of gases at given loadings. Since these MOFs were highly CH₄ selective, H₂ loadings were very low compared to CH₄ loadings. The size of the simulation volume was increased to 4 × 4 × 4 to contain enough particles to increase the statistical accuracy of EMD simulations. The ratio of self-diffusivities of gases ($D_{self,CH_4}/D_{self,H_2}$) was used to define the diffusion selectivity of MOFs. Membrane selectivity was calculated as the multiplication of adsorption selectivity and diffusion selectivity at a feed pressure of 10 bar and permeate pressure of vacuum as described in the literature.¹⁹

2.3. Calculating Adsorbent Properties of MOFs. We calculated adsorption selectivities of MOFs for CH₄/H₂ separations using both single-component and mixture simulation data. Results obtained from molecular simulations of single-component gases (CH₄ and H₂) were used to predict intrinsic selectivity of MOFs, also known as ideal selectivity. Ideal adsorption selectivity (IS_{ads}) of component i from component j was calculated as the ratio of single-component adsorbed amounts of gases (c_i^{pure}):

$$IS_{ads(i/j)} = \frac{c_i^{pure}}{c_j^{pure}} \quad (1)$$

Results obtained from molecular simulations of binary gas mixtures (CH₄/H₂) were used to predict mixture selectivity of MOFs. Mixture adsorption selectivity (S_{ads}) was calculated as the ratio of adsorbed amounts of components in their binary mixtures, where $c_i^{mixture}$ is the adsorbed loading of component i in the mixture calculated from GCMC simulations and y_i is the bulk composition of component i in the mixture:

$$S_{ads(i/j)} = \frac{c_i^{mixture}/c_j^{mixture}}{y_i/y_j} \quad (2)$$

GCMC simulations were performed at various pressures, 0.01, 1, 10, 20, 65, and 100 bar at 298 K to compute ideal and mixture selectivities.

Adsorption selectivity and working capacity are the two important parameters that define the efficiency of materials in adsorption-based gas separations. Working capacity (Δc_i), was defined as the difference between the adsorbed amounts of gas at the adsorption and desorption pressures:

$$\Delta c_i = c_i^{mixture,ads} - c_i^{mixture,des} \quad (3)$$

The sorbent selection parameter (S_{sp}) of each MOF was calculated as defined in the literature⁴⁰ where S_{ads} (S_{des}) represents selectivity calculated at adsorption (desorption) pressure and Δc_i represents working capacity of component i :

$$S_{sp} = (S_{ads(i/j)})^2 / (S_{des(i/j)}) \cdot \Delta c_i / \Delta c_j \quad (4)$$

S_{sp} provides useful information about the overall separation performance of an adsorption process because including the ratio of working capacities increases the sensitivity of this dimensionless parameter.⁴¹

Percent regenerability, $R\%$, is an important parameter that evaluates practical usage of an adsorbent for cyclic PSA processes. It was defined as the ratio of working capacity of the strongly adsorbed component to the amount of adsorbed gas:⁴⁰

$$R\% = \frac{\Delta c_i}{c_i^{mixture,ads}} \cdot 100 \quad (5)$$

All calculations were carried out at room temperature. To compute Δc_i , S_{sp} , and $R\%$, adsorption and desorption pressures were set to 10 and 1 bar, respectively, since most of the adsorption-based separations in industry are performed under these conditions. The bulk gas composition of the mixture was set as equimolar in all calculations.

3. RESULTS AND DISCUSSION

3.1. Comparing Ideal and Mixture Adsorption Selectivities of MOFs. Selectivity is the most critical factor to assess adsorption-based separation performances of MOFs.

Figure 1. Comparison of ideal and mixture selectivities of MOFs in CH_4/H_2 separations at (a) 0.01, (b) 1, (c) 10, (d) 20, (e) 65, (f) 100 bar. The red line is the $x = y$ line to guide the eye.

In most experimental studies, single-component adsorption isotherms of gases in MOFs are measured and the selectivity of MOF is simply calculated as the ratio of adsorbed amounts of

single-component gases. This selectivity is known as ideal selectivity and it represents the intrinsic separation capacity of a material. Ideal selectivity may significantly differ from mixture

Figure 2. Comparison of CH_4/H_2 selectivity predictions of our model³⁹ with the results of GCMC simulations at (a) 1, (b) 5, (c) 10, (d) 20, (e) 65, (f) 100 bar. The red line is the $x = y$ line to guide the eye.

selectivity when competition effects between two gas species become dominant.⁴² We computed both ideal CH_4/H_2 selectivities and mixture selectivities of MOFs using single-component and mixture GCMC simulations, respectively. Figure 1 shows comparison of ideal and mixture selectivities

of 250 MOFs at six different pressures, 0.01, 1, 10, 20, 65, and 100 bar at room temperature. All MOFs are CH_4 selective since H_2 has weaker interactions with the framework atoms compared to CH_4 . Figure 1a shows that ideal and mixture selectivities are almost the same at a pressure close to zero, 0.01

bar. The coefficient of multiple determination (R^2) between ideal and mixture selectivities is 0.9996 at 0.01 bar. The deviation between ideal and mixture selectivities increases as the pressure increases as shown in Figures 1 (b-f). The value of R^2 decreases to 0.8 at 1 bar and becomes less than 0.4 at higher pressures. This deviation can be explained by the multi-component mixture effects which become important at high pressures. As the loading increases gas molecules compete with each other for the same adsorption sites. Adsorption favors CH_4 over H_2 in the mixture and the more strongly adsorbing CH_4 molecules exclude weakly adsorbing H_2 molecules in the pores. As a result, mixture selectivities become always higher than the ideal selectivities as shown in Figure 1, except 0.01 bar where two selectivities are identical. Figure 1 suggests that ideal selectivity can be used to assess separation performance of MOFs at low pressures (≤ 1 bar). As pressure increases, ideal selectivity underestimates the “real” (mixture) selectivity of MOFs in CH_4/H_2 separation. This means screening new materials based on ideal selectivity calculated at low pressures may lead to wrong conclusions about the materials’ performances at high pressures.

We previously showed the good agreement between our predicted ideal selectivities and experimentally reported ideal selectivities of several ZIFs.¹⁰ In this work, we also compared our predicted ideal selectivities with the experiments for several other MOFs. Experimental ideal selectivities of MOFs were determined from the corresponding single-component adsorption isotherms of CH_4 and H_2 . To extract the exact uptake at the desired pressure, interpolation was performed on the experimental gas uptake isotherms. For NU-125⁴³ and MOF-5,⁴⁴ experimental ideal selectivities were found as 9.0 and 5.2 at 5 bar, whereas our simulation results were 9.4 and 5.5, respectively, under the same conditions. For ZIF-8⁴⁴ and NU-140⁴⁵ experimental ideal selectivities were 3.6 and 3.2 at 50 bar which were predicted as 4.4 and 4.1 by our simulations, respectively. Experiments for MOF-5 and ZIF-8 were reported at 300 K, whereas all our molecular simulations were performed at a slightly lower temperature, 298 K. These comparisons validate the accuracy of our molecular simulations.

There was no experimental CH_4/H_2 mixture adsorption data of MOFs in the literature therefore we were not able to compare our mixture selectivities with the experiments. We compared the mixture selectivities calculated from our GCMC simulations with the ones calculated by Wu et al.²⁵ for 10 well-known MOFs that are common in both simulation studies. Comparison of the simulation results is shown in Supporting Information Figure S1. Our simulated mixture selectivities showed very good agreement with the selectivities calculated by Wu et al.²⁵ For ZIF-6, MOF-5, PCN-6, HKUST-1, and ZIF-8, we calculated selectivities as 13.5, 6.8, 7.8, 14.6, and 19.1 which were reported as 12.4, 6.2, 8.8, 15.1 and 17.8, respectively by Wu et al.²⁵ Our calculated selectivities of 250, 236, and 120 for CUK-2 (which was identified by Wu et al. as the top performing MOF for CH_4/H_2 separation) agreed well with their calculated values of 267, 252, and 126 at 0.01, 1, and 10 bar, respectively. The small differences are due to the different force fields used in molecular simulations. We used UFF for most MOFs whereas Wu et al.²⁵ used the Dreiding force field. In fact, this comparison suggests that choice of the force field does not have a significant effect on the predicted selectivities of MOFs.

3.2. Predicting Adsorption Selectivity of MOFs Using Simple Models. Molecular simulations are highly useful for

screening a large number of materials and revealing structure–function correlations that would be helpful in guiding the design of new MOFs. However, simulations of gas mixtures can be time-consuming especially if the number of materials to be studied is high. Simple models that can make accurate predictions for adsorption selectivity of MOFs based on the structural properties of materials are very useful to get an initial estimate about the separation performance of materials. We recently examined the relation between CH_4/H_2 adsorption selectivity of several PCNs’ (porous coordination networks) and structural/chemical properties of these materials such as pore volume, surface area, isosteric heat of adsorption.³⁹ We showed that there is a very good correlation between CH_4/H_2 adsorption selectivity of PCNs and three parameters, geometric pore volume (V_{pore}), surface area (A_{surface}), and inverse of the difference of isosteric heats of adsorption of components in the mixture ($1/\Delta Q_{\text{st}}$). On the basis of this result, we developed a simple model that can predict PCNs’ CH_4/H_2 selectivities based on the material’s V_{pore} , A_{surface} , and $1/\Delta Q_{\text{st}}$.³⁹

$$S_{\text{ads}} = a \cdot V_{\text{pore}}^b + c \cdot A_{\text{surface}}^d + e \cdot (1/\Delta Q_{\text{st}})^f + 1 \quad (6)$$

In this model, a – f represent the model coefficients which were listed in our previous report.³⁹ The isosteric heat of adsorption at infinite dilution (ΔQ_{st}^0) is an important factor that is used to describe the intrinsic adsorption affinity of MOFs for gas molecules. To use eq 6 at various pressures rather than only at infinite dilution, we used ΔQ_{st} values calculated at the corresponding partial pressures of CH_4/H_2 mixtures. For example, when an equimolar CH_4/H_2 mixture was studied at an adsorption pressure of 10 bar, the Q_{st} values were calculated at 5 bar using GCMC simulations. It is important to note that one does not necessarily need to perform GCMC simulations to calculate Q_{st} to use it in eq 6. We recently developed simple linear regression models which can estimate Q_{st} by using any of the other easily measurable structural parameters (such as pore volume, pore diameter) at considered pressures.²⁸ By using these models, Q_{st} can be predicted for any MOF at any pressure without performing GCMC simulations.

We used eq 6 to predict CH_4/H_2 selectivity of 250 MOFs considered in this study. Figure 2 compares predictions of the model with the results of direct GCMC simulations for all MOFs at various pressures (1, 5, 10, 20, 65, 100 bar). There is a good agreement between the model predictions and simulation results. The R^2 values are 0.94, 0.93, 0.91, and 0.85 at 1, 5, 10, and 20 bar, respectively. These values decrease as the pressure increases as can be seen from Figure 2. This is expected since the structural properties of the materials become less important in determining separation performance as the adsorbate loading increases. At low loadings, adsorbate–MOF interactions are dominant and the structural properties of the MOFs are important. At higher loadings adsorbate–adsorbate interactions become much more pronounced than adsorbate–MOF interactions. Predictions of the model are very good specifically at low pressures indicating that eq 6 can be used to get an initial estimate about the low-pressure adsorption selectivity of MOFs before performing extensive calculations.

Adsorption selectivity favors CH_4 at low pressures since CH_4 is energetically preferred over H_2 . At higher pressures, adsorption selectivity for CH_4 over H_2 decreases for most MOFs because entropic effects come into play and favor H_2 adsorption. There are 18 MOFs in our database that show relatively constant CH_4/H_2 selectivities in the pressure range of

Figure 3. Comparison of CH_4/H_2 selectivity predictions of the model suggested by Wu et al.²⁵ with our GCMC simulations at (a) 0.01 and (b) 20 bar.

Figure 4. (a) Relation between CH_4/H_2 selectivity of MOFs and isosteric heat of adsorption difference of gases calculated at 0.01 bar. The red line is obtained from eq 9. (b) Comparison of CH_4/H_2 selectivity predictions of model suggested by Yang et al.¹¹ with our GCMC simulations at 0.01 bar.

0.01 to 100 bar. This trend is mostly seen in PCNs and ZIFs such as PCN-20, PCN-80, ZIF-10 and ZIF-60 with selectivities of 8, 7, 11 and 11, respectively. The CH_4/H_2 selectivities of these materials do not significantly change as the pressure increases since both CH_4 and H_2 adsorption increase in similar proportion. Equation 6 predicts this constant selectivity well because the ΔQ_{st} values of these MOFs also remain constant throughout a large pressure range. There are four other MOFs (ALICII, ALICEE, LARVIL, XIJNUA) that also have relatively constant selectivities (6, 10, 14, 2, respectively), however eq 6 overestimates adsorption selectivities of these MOFs. This can be explained with the following discussion: ALICII, ALICEE, and LARVIL have very low pore volumes ($\sim 0.2 \text{ cm}^3/\text{g}$) compared to other MOFs. In eq 6, pore volume and adsorption selectivity are inversely related. Therefore, eq 6 overestimates adsorption selectivity of these MOFs. XIJNUA has a much higher pore volume ($1.05 \text{ cm}^3/\text{g}$) but its ΔQ_{st} value (3.09 kJ/mol) is unusually small compared to ΔQ_{st} values of other

MOFs. Since ΔQ_{st} and adsorption selectivity are also inversely related, the model overestimates this MOF's selectivity.

Finally, it is important to highlight that eq 6 was initially developed by studying only 20 different PCNs representing a small variety of topology and composition.³⁹ In this study, we considered 250 different MOFs including several subgroups such as IRMOFs, ZIFs, COFs, PCNs, and bio-MOFs. The good agreement between model predictions and molecular simulations suggest that 20 PCNs initially used to develop the model was a good subset to represent a large variety of MOFs. Since this model was developed for 20 materials and found to give good predictions for 250 different materials, it may be also concluded that MOFs have some common structure-performance relationships.

Two other models that were recently suggested in the literature to predict adsorption selectivity of nanoporous materials were also examined to understand which parameters are crucial in determining adsorption selectivity of MOFs. Wu et al.²⁵ recently described a parameter called “adsorbility” and

Figure 5. CH₄/H₂ selectivity vs CH₄ working capacity calculated in units of (a) mol/kg and (b) mol/L for MOFs.

showed that there is a good correlation between CH₄/H₂ selectivity and the inverse of difference in adsorbility of gases represented as $1/\Delta\text{AD} = \varphi/\Delta Q_{\text{st}}^0$ where φ represent porosity of MOFs. They suggested the following correlations relating CH₄/H₂ selectivity of MOFs to $1/\Delta\text{AD}$ at 0.01 and 20 bar, respectively:

$$S_{\text{ads}} = 0.0031 \cdot (1/\Delta\text{AD})^{-3.1} + 1 \quad (7)$$

$$S_{\text{ads}} = 0.1268 \cdot (1/\Delta\text{AD})^{-1.78} + 1 \quad (8)$$

We applied these models to 250 MOFs examined in this work and calculated R^2 values as 0.59 at 0.01 bar and 0.42 at 20 bar as shown in Figure 3. The R^2 value calculated at 20 bar was lower than the one calculated at 0.01 bar because ΔQ_{st}^0 represents the affinity of MOFs to gas molecules at infinite dilute loading. Therefore, low-pressure selectivity correlates better with $1/\Delta\text{AD}$. Comparison of results shown in Figures 2 and 3 suggests that the model that includes structural properties such as surface area and pore volume in addition to the difference of isosteric heats of adsorption of components is more accurate in predicting adsorption selectivity of MOFs. The model that employs ΔQ_{st} calculated at the partial pressures of gases, eq 6 gives better predictions at high pressures than the models employing ΔQ_{st}^0 , eqs 7 and 8.

Another model that was derived based on the Langmuir adsorption theory relates gas selectivity and isosteric heat of adsorption differences of gases as follows, where R is the gas constant and T is temperature:¹¹

$$\ln S_{\text{ads}} = -0.8558 + \Delta Q_{\text{st}}^0/RT \quad (9)$$

This equation should be suitable for all the physical adsorption separation of gas mixtures in porous materials since it has a solid theoretical basis. Yang et al.¹¹ used this model to predict CO₂/H₂, CO₂/N₂, CO₂/CH₄, and CH₄/H₂ selectivities of four different PAFs (porous aromatic frameworks). We showed the adsorption selectivities of MOFs studied in this work as a function of ΔQ_{st}^0 together with the line obtained from eq 9 in Figure 4a. Equation 9 well predicts CH₄/H₂ selectivity of MOFs which have low ΔQ_{st}^0 values. Predictions deviate from the simulated selectivity results for MOFs having high ΔQ_{st}^0 values. In other words, if the difference between the isosteric

heat of adsorption of two gases is large at low loadings, then eq 9 overpredicts the material's selectivity. To show this point, mixture selectivities calculated directly from GCMC simulations were compared with the selectivity predictions of eq 9 by grouping the MOFs based on their ΔQ_{st}^0 values in Figure 4b. Adsorption selectivities of MOFs that have ΔQ_{st}^0 values ≤ 12 kJ/mol are accurately predicted by eq 9, whereas selectivities of MOFs that have ΔQ_{st}^0 values between 12 and 20 kJ/mol are overpredicted.

Models given in eqs 7 and 9 were developed to predict intrinsic separation ability of materials at low pressures, whereas the model we suggested eq 6 is able to predict CH₄/H₂ selectivity of MOFs at any pressure since pressure is a hidden parameter accounted in ΔQ_{st} . Identifying a MOF exhibiting high adsorption selectivity at low pressure such as 0.01 bar does not guarantee that the high selectivity of material will be preserved at an industrial operating pressure such as 10 bar. In fact, adsorption selectivity of most MOFs drops significantly as the pressure increases as we discussed before. Figure S2 shows the ratio of CH₄/H₂ selectivity of MOFs calculated at 0.01 bar to the one calculated at 10 bar. This ratio is less than 2 for 209 MOFs. However, there are 41 MOFs for which this ratio is much higher than 2 and even increases up to 8. For example, a MOF named as GIQHAQ exhibits CH₄ selectivity of 180 at 0.01 bar but this value drops to 23 at 10 bar. Therefore, screening the MOFs' adsorption selectivities not at low pressures but at the operating pressure of the adsorption process is much more useful to prevent overestimation of the materials' separation performances.

Finally, it is important to note that the models we discussed above attempt to correlate selectivity with only a few properties. However, adsorption selectivity of a material is determined by the interplay of various factors. For example, chemical composition and topology of MOFs should strongly affect the affinity of materials for specific gas molecules but these are not specifically considered in the simple models that we discussed. The aim of these models must be seen to screen a large number of materials in an efficient manner and accurately identify the highly selective ones for further experimental and theoretical examination.

3.3. Assessing Adsorbent Properties of MOFs. Figure 5a shows the two important factors that determine adsorption-

based separation performance of materials, mixture selectivity, and working capacity. Our results show that a significant number of MOFs (218) have CH_4/H_2 selectivities less than 50 and CH_4 working capacities between 1 and 3 kg/mol. We defined a reference performance curve of $S_{\text{ads}} \cdot \Delta c_{\text{CH}_4} = 150$, which we utilized to separate high and low performance regions within the MOF search space following Smit's group⁴⁶ who defined a reference curve in screening zeolites for ethane/ethene separation. The choice of 150 in this work is intuitively arbitrary assuming $S_{\text{ads}}(\text{CH}_4/\text{H}_2) = 50$ and $\Delta c_{\text{CH}_4} = 3$ mol/kg, only to provide a reference curve to quantitatively define a number of promising MOFs. A total of 32 MOFs were identified out of 250 as the top performing structures exceeding the reference curve. It is interesting to see that several MOFs with high CH_4 selectivity (>100) exhibit low CH_4 working capacity (<1 mol/kg), limiting their practical usage. Some others, on the other hand, are promising in terms of working capacity (>4 mol/kg) but they have moderate selectivities (around 50). Traditional zeolites CHA, LTA, and ITQ-29 were also included in Figure 5a to compare the separation performance of MOFs with zeolites. The selectivity and working capacity of these zeolites were previously calculated at 10 bar, 300 K using molecular simulations.⁴⁷ Many MOFs outperform these well-known zeolites in terms of selectivity and working capacity indicating that MOFs can be better candidates than zeolites in adsorption-based separation of a CH_4/H_2 mixture. In Figure 5b, we used working capacity in terms of mol/L to compare the separation performances of MOFs with 5A zeolite, coal carbon, silica gel, activated alumina, and coconut carbon. The adsorption data for these five nanoporous materials were experimentally measured. Their selectivities were calculated from Henry's law constants at 303 K, and working capacities were reported between ~ 3 and 0.5 bar.⁴⁸ MOFs have significantly larger CH_4 working capacities than these nanoporous materials which can be attributed to larger pore volumes of MOFs. There are several MOFs that exhibit extremely large selectivities (>100) compared to these nanoporous materials.

Figure 6 shows S_{sp} values and adsorption selectivities of MOFs calculated at an adsorption pressure of 10 bar and desorption pressure of 1 bar. A significant portion of MOFs is located in a region where selectivity is less than 50 and S_{sp} is less than 2500. The most promising adsorbent candidates are positioned at the top right corner of the figure. Two MOFs,

Figure 6. S_{sp} vs CH_4/H_2 selectivity of MOFs.

IPIDAN and SUGWEX03 exhibit extraordinarily high S_{sp} (24078 and 17328, respectively) and CH_4 selectivity (204 and 127, respectively). Among the MOFs we studied, IPIDAN has the highest adsorption selectivity and therefore it has the highest S_{sp} value. SUGWEX03 is the eighth material among 250 of MOFs in terms of its adsorption selectivity but it ranks as number two according to its S_{sp} value. This is due to the high CH_4/H_2 working capacity ratio of SUGWEX03. As eq 4 shows, S_{sp} considers the ratio of working capacity of the strongly adsorbed gas component to the weakly adsorbing one. Since SUGWEX03 has a large CH_4 working capacity and low H_2 working capacity, it was identified as a promising adsorbent with a high S_{sp} value. As Figure 6 shows there are six other MOFs that have higher adsorption selectivity than SUGWEX03 (except IPIDAN), but they are not as promising as SUGWEX03 due to their lower working capacity ratios and S_{sp} values. Widely studied MOFs in the literature such as MOF-5, HKUST-1, and ZIF-8 exhibit low S_{sp} values compared to many other MOFs.

High percent regenerability ($R\%$) is desired for practical applications of adsorbents. Tong et al.⁴⁹ calculated $R\%$ of 46 COFs for CO_2/N_2 separation and reported that 42 COFs have $R\%$ between 80 and 90%. We calculated $R\%$ of 250 MOFs for CH_4/H_2 separation and found out that only 133 MOFs have $R\%$ between 80 and 90%. In other words, almost half of the MOFs suffer from low $R\%$ values. The relation between $R\%$ and adsorption selectivity of MOFs is shown in Figure 7.

Figure 7. $R\%$ vs CH_4/H_2 selectivity of MOFs. Red dotted line marks 80% regenerability.

Highly promising materials must be located at the top right corner of this figure showing both high selectivity and $R\%$. There is a negative correlation between regenerability and selectivity for most MOFs. As the selectivity increases, $R\%$ decreases. Several MOFs exhibit very high selectivities (>100) but their $R\%$ values are less than 50% suggesting that these materials may not find place in practical applications. At that point, it is good to discuss $R\%$ of MOFs that were identified to show high S_{sp} and selectivity in Figure 6. One of the promising MOFs, SUGWEX03 has a reasonable regenerability, 65%. However, most of the MOFs that were identified as highly promising materials as we will discuss below (i.e., IPIDAN, PEQHOK, DORDUK, PAVLUU, and EMIVAY) have $R\%$ values lower than 40%. This is due to the similar CH_4

adsorption capacities of MOFs at adsorption (10 bar) and desorption (1 bar) pressures. In other words, CH₄ reaches to saturation at around 1 bar in these materials. Therefore, CH₄ uptake capacity of these MOFs is very similar at adsorption (10 bar) and desorption pressures (1 bar), leading to low working capacities and low regenerabilities. This result can be attributed to the low pore volumes (around 0.35 cm³/g) of these MOFs which become saturated with CH₄ at low pressures.

Although most of the promising MOFs that show high adsorption selectivity have low regenerability, many MOFs having moderate selectivity and high regenerability are present. For example, FEHCOM, DIDBID, and ISOJOQ have CH₄/H₂ selectivities of 65, 57, and 57 with R% of 79%, 77%, and 73%, respectively. These materials do not seem to have extraordinarily large adsorption selectivities; however, having high regenerability makes them promising candidates for practical applications. Among the most commonly used MOFs, we identified some having low selectivity but high regenerability and some having the opposite. For example, CUK-2, which was identified by Wu et al.²⁵ as the top performing MOF for CH₄/H₂ separation, is a highly selective material with a CH₄/H₂ selectivity of 120 at 10 bar. However, its R% is quite low, 38%. On the other hand, PCN-14 shows high regenerability, 81% but its selectivity can be considered to be moderate, 28 at 10 bar. One of the most commonly studied MOFs in the literature, MOF-5, has a very promising regenerability, 90%, but its CH₄/H₂ selectivity is quite low, 7. These examples suggest that there are several criteria that need to be considered when selecting a MOF for an adsorption-based gas separation application, and selectivity should not be the only parameter in assessing the performance of adsorbents.

The top 10 MOFs showing the highest CH₄/H₂ separation performance are listed in Table 1. These materials were ranked

Table 1. Adsorption-Based Separation Performances of Top Performing Materials

REFCODE	S_{sp}	ΔC_{CH_4} (mol/kg)	R%	S_{ads}		
				0.01 bar	1 bar	10 bar
IPIDAN	24078	0.92	35.8	280.2	257.3	204.1
SUGWEX03	17328	3.18	64.4	106.5	120.5	126.6
CAYBAH	9194	1.50	67.9	102.0	106.7	100.3
PEQHOK	8430	0.82	39.8	275.1	235.3	146.1
DORDUK	7497	0.62	32.8	346.3	313.8	166.5
PAVLUU	7353	0.98	34.8	307.6	298.8	160.1
SARBOE	6964	1.80	41.3	238.6	223.9	134.7
EMIVAY	6534	1.06	30.4	241.3	265.7	151.1
GUSLUC	6069	1.11	47.5	291.7	215.3	124.2
WEMFUR	5963	1.34	50.6	175.6	165.3	109.4

based on their S_{sp} values, and other criteria such as selectivity, working capacity, and regenerability were also listed in Table 1. All these materials show very high CH₄/H₂ adsorption selectivities greater than 100. This is due to the low H₂ uptake of MOFs when an equimolar CH₄/H₂ mixture is considered. Figure S3 shows that H₂ uptake of highly selective MOFs decreases significantly in the presence of CH₄, whereas CH₄ uptake remains almost unchanged in the presence of H₂. This suggests that there is a significant competition between CH₄ and H₂ molecules resulting in the dominance of CH₄ molecules filling the adsorption sites. This dominance of CH₄ molecules over H₂ results in high CH₄/H₂ selectivity which enables us to identify these MOFs as the top performing materials. For comparison, we also showed single-component and mixture adsorption isotherms of gases in a commonly studied MOF, MOF-5 in Figure S3. Both CH₄ and H₂ uptake decrease in similar amounts in the binary mixture compared to pure gas uptakes in the case of MOF-5. Therefore, MOF-5 does not have high adsorption selectivity. To examine whether these MOFs are also promising at pressures higher than 10 bar, we investigated the change in the selectivities between 10 and 65 bar. Selectivities of all MOFs decrease with increasing pressure, however DORDUK and EMIVAY showed a significant decrease of ~70% in their selectivities when the pressure was increased from 10 to 65 bar. CAYBAH is one of the promising MOF candidates which only shows 29% decrease when the pressure is increased from 10 to 65 bar.

3.4. Assessing Membrane Selectivity of MOFs.

Membrane selectivity is estimated as the multiplication of adsorption and diffusion selectivity as defined in the literature.¹⁹ Performing mixture EMD simulations to calculate diffusion selectivity is challenging and computationally costly. Therefore, we only calculated diffusion selectivity of MOFs that already showed high adsorption selectivity. We simply thought that promising membrane materials can be identified if the MOFs that show the highest adsorption selectivity also exhibit high diffusion selectivity. We investigated membrane-based separation potential of the most promising MOFs listed in Table 1. We computed self-diffusion coefficients of CH₄ and H₂ in the top five MOFs that exhibit the highest S_{sp} , namely IPIDAN, SUGWEX03, CAYBAH, PEQHOK, and PAVLUU. The self-diffusion coefficients of CH₄ and H₂, the ratio of these diffusivities which is defined as the diffusion selectivity ($S_{diffusion}$) and the multiplication of adsorption and diffusion selectivities which is defined as the membrane selectivity ($S_{membrane}$) are all given in Table 2. Results showed that H₂ diffuses faster than CH₄ in all MOFs as expected. There are two reasons for the faster diffusion of H₂: (a) H₂ is a lighter and smaller molecule than CH₄. (b) Since CH₄ adsorbs more strongly into the pores of MOFs, it moves slower than H₂. In CAYBAH, SUGWEX03, and PAVLUU, gas diffusivities are in the orders of 10⁻⁵–10⁻⁴ cm²/s. The limiting/largest pore sizes

Table 2. Adsorption, Diffusion and Membrane Selectivities of Top Performing Materials^a

REFCODE	S_{ads}	D_{self,CH_4} (cm ² /s)	D_{self,H_2} (cm ² /s)	$S_{diffusivity}$	$S_{membrane}$
IPIDAN	204.06	4.20×10^{-8}	1.77×10^{-7}	0.24	48.37
SUGWEX03	126.60	1.68×10^{-5}	1.85×10^{-4}	0.09	11.53
CAYBAH	100.31	2.41×10^{-5}	4.79×10^{-5}	0.50	50.52
PEQHOK	146.14	$< 10^{-8}$	1.61×10^{-7}		
PAVLUU	160.1	1.23×10^{-4}	1.51×10^{-4}	0.81	130.21

^aData for DORDUK is not shown in the table since none of the gases is able to diffuse in the narrow pores of this material.

of these MOFs were calculated as 3.64/4.85, 3.81/5.77, 4.09/4.45 Å using Poreblazer code. IPIDAN and PEQHOK have narrower pore limiting diameters (2.99/5.09 Å and 2.37/5.07 Å), therefore both gases diffuse slower in these MOFs in the orders of 10^{-8} – 10^{-7} cm²/s. Diffusion of CH₄ was not accessible on the nanosecond time scales accessible using EMD ($<10^{-8}$ cm²/s) in the narrow pores of PEQHOK. Therefore, we did not report diffusion and membrane selectivity for this material. In all these MOFs, adsorption selectivity favors CH₄ (CH₄/H₂ selectivity >1) whereas diffusion selectivity favors H₂ (CH₄/H₂ selectivity <1). Since membrane selectivity is predicted as the multiplication of adsorption and diffusion selectivities, predicted membrane selectivities for CH₄ are lower than the adsorption selectivities. In other words, these MOFs would be much more efficient in adsorption-based separations than in kinetic-based separations. For example, IPIDAN exhibits very high adsorption selectivity for CH₄ (204) but its membrane selectivity drops to 48 under the same conditions. Similarly, membrane selectivity of CAYBAH was predicted as 50.5 almost half of its adsorption selectivity, 100.3. PAVLUU has the highest membrane selectivity (130.2) which only drops ~20% compared to its adsorption selectivity. Among the MOFs that we examined as membranes, we did not find any structure that is H₂ selective. Of course, it would be very interesting to identify MOFs where diffusion selectivity for H₂ overcomes the adsorption selectivity for CH₄. It is also important to note that these membrane selectivities, although lower than adsorption selectivities, are very promising compared to the reported selectivities of many other MOF membranes. We previously showed that CH₄/H₂ membrane selectivities of most ZIFs and COFs are generally less than 10 for equimolar mixtures at a membrane feed pressure of 10 bar.^{21,22} Membrane selectivities of zeolites were predicted to be between 0.01 and 10 for separation of equimolar CH₄/H₂ mixtures at 1–20 bar.⁴⁷ On the basis of these comparisons, we can conclude that MOFs exhibiting high adsorption selectivity can be efficiently used for membrane-based separation of CH₄/H₂ mixtures.

Finally, it is important to clearly describe the limitations of the computational approach that we used to screen MOFs for CH₄/H₂ separation. In all molecular simulations, MOF framework is assumed to be rigid in its reported crystallographic structure. Although this assumption has been used almost in all molecular simulation studies of MOFs in the literature, there may be MOFs for which framework flexibility is important. The main aim of our calculations is to demonstrate the potential value of a material using an efficient computational screening approach. As suggested in the literature once a material is identified to be promising, molecular simulations can be performed for a range of possible crystal structures to improve the precision of initial screening.²⁶ A related issue is that we used the solvent-free MOF database of Snurr et al.²⁷ A promising adsorbent material must have structural framework stability after the solvent molecules are evacuated. This issue is more likely to be examined experimentally. The value of our computational work is that it can provide a motivation to perform detailed experimental studies for the thermal and structural stability of promising materials. We collected stability information for the top performing 10 MOFs listed in Table 1 from their corresponding experimental synthesis studies. CAYBAH,⁵⁰ EMIVAY,⁵¹ and WEMFUR⁵² were reported to exhibit high thermal stability and permanent porosity. GUSLUC⁵³ and PAVLUU⁵⁴ were reported to be air stable,

and PAVLUU can retain its crystalline integrity at ambient conditions. PEQHOK⁵⁵ shows exceptional thermal stability and can be stable in common organic solvents and even in water beyond 1 week, which makes it an ideal candidate for gas separations. SUGWEX03⁵⁶ was reported to retain structural integrity at ambient condition after removal of the solvent. There is one MOF, SARBOE,⁵⁷ reported to be kinetically stable but thermodynamically metastable. No specific information was available for the stability of the two top performing MOFs, DORDUK and IPIDAN.

4. CONCLUSION

It is challenging to identify promising MOFs for gas separation applications due to the presence of very large number of distinct MOF structures. In this study, molecular simulations were used to assess CH₄/H₂ separation performance of MOFs and the top performing materials were identified. We showed that several MOFs that are identified to have high adsorption selectivity may not be promising due to their low regenerability. In other words, we showed that selecting MOFs purely based on their adsorption selectivity may not be a good strategy. Several MOFs can outperform well-known zeolite adsorbents by exhibiting higher CH₄/H₂ selectivity and working capacity under the same conditions. It was also shown that ideal selectivity is a good indicator for separation performance of MOFs at low pressures (≤ 1 bar); however, it underestimates the “real” (mixture) selectivity of MOFs at high pressures for CH₄/H₂ separation.

Interactions between gas molecules and MOFs are determined by the interplay of several parameters such as chemical composition, topology, surface area, and pore volume of materials. Among many parameters, surface area and pore volume are perhaps the simplest ones to be measured both by experiments and simulations. Therefore, we used a simple model that can predict the CH₄/H₂ selectivity of MOFs once the surface area and pore volume are defined in addition to the inverse of the difference of heat of adsorption values. Results show that this simple model can be used to accurately assess the adsorption-based separation performance of MOFs at 1, 5, 10, and 20 bar. We identified the top performing MOFs for adsorption-based CH₄/H₂ separation by ranking them based on their S_{sp} values. The kinetic separation performance of these MOFs was also examined. Results showed that MOFs exhibiting high adsorption selectivity can be also efficiently used for membrane-based separation of CH₄/H₂ mixtures revealing the kinetic separation potential of MOFs. Finally, it is important to note that we only examined a fraction of the MOFs that are reported in the CCDC; therefore, we believe that many more MOFs which may show better separation performance may exist in the database. The computational approach that we described here can be used to further screen a large number of MOFs not only for CH₄/H₂ separation but also for other gas separation applications.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01901.

The list of studied MOFs, comparison of our simulated CH₄/H₂ mixture selectivities with the ones simulated by Wu et al., the ratio of CH₄/H₂ selectivity of MOFs calculated at 0.01 bar to the one at 10 bar, single-

component and equimolar binary mixture adsorption isotherms of gases in selected MOFs. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: skeskin@ku.edu.tr. Tel.: +90 (212) 338-1362.

Author Contributions

[†]Y.B. and K.B.S. contributed equally to this work.

Notes

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