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Computational Screening of MOFs for Acetylene Separation

*Ayda Nemati Vesali Azar and Seda Keskin**

Department of Chemical and Biological Engineering, Koc University, Istanbul, Turkey

Efficient separation of acetylene (C_2H_2) from CO_2 and CH_4 is important to meet the requirement of high-purity acetylene in various industrial applications. Metal organic frameworks (MOFs) are great candidates for adsorption-based C_2H_2/CO_2 and C_2H_2/CH_4 separations due to their unique properties such as wide range of pore sizes and tunable chemistries. Experimental studies on the limited number of MOFs revealed that MOFs offer remarkable C_2H_2/CO_2 and C_2H_2/CH_4 selectivities based on single-component adsorption data. We performed the first large-scale molecular simulation study to investigate separation performances of 174 different MOF structures for C_2H_2/CO_2 and C_2H_2/CH_4 mixtures. Using the results of molecular simulations, several adsorbent performance evaluation metrics, such as selectivity, working capacity, adsorbent performance score, sorbent selection parameter, and regenerability were computed for each MOF. Based on these metrics, the best adsorbent candidates were identified for both separations. Results showed that the top three most promising MOF adsorbents exhibit C_2H_2/CO_2 selectivities of 49, 47, 24 and C_2H_2/CH_4 selectivities of 824, 684, 638 at 1 bar, 298 K and these are the highest C_2H_2 selectivities reported to date in the literature. Structure-performance analysis revealed that the best MOF adsorbents have pore sizes between 4 and 11 Å, surface areas in the range of 600–1,200 m^2/g and porosities between 0.4 and 0.6 for selective separation of C_2H_2 from CO_2 and CH_4. These results will guide the future studies for the design of new MOFs with high C_2H_2 separation potentials.

Keywords: metal organic frameworks, C_2H_2 separation, adsorption, selectivity, molecular simulation

Edited by:
Alexei Lapkin,
University of Cambridge,
United Kingdom

Reviewed by:
Nils E. R. Zimmermann,
Lawrence Berkeley National Laboratory (LBNL), United States
Ravichandar Babarao,
RMIT University, Australia

Correspondence:
Seda Keskin
skeskin@ku.edu.tr

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INTRODUCTION

Metal organic frameworks (MOFs), nanoporous materials that are composed of metal clusters connected with organic linkers, have attracted significant interest in the last decade. MOFs offer a wide range of pore sizes, permanent porosities, very large surface areas, and good chemical stabilities (Li et al., 1999; Eddaoudi et al., 2002). The most important characteristic of MOFs is that their physical, chemical and structural properties can be tuned during synthesis. This controllable synthesis leads to a large diversity of materials having different geometry, pore size, and chemical functionality (Mondloch et al., 2013). Due to these advantageous physical and chemical properties, MOFs have emerged as strong alternatives to traditional nanoporous materials in various gas separation applications. MOFs have been widely examined for CO_2 separation because of the growing environmental concerns on the removal of CO_2 from natural gas (CO_2/CH_4), flue gas (CO_2/N_2), and from other gases (CO_2/H_2). Experimentally measured selectivities and gas uptake capacities of several MOFs for separation of CO_2 from CH_4 and N_2 have been reported and results showed that MOFs can be strong alternatives to traditional porous materials in CO_2 separations (Li et al., 2011). Comparison of CO_2 separation performances of MOFs, zeolites and activated carbons showed that CO_2/N_2 selectivity changes from low in zeolites to moderate in carbon-based absorbents and becomes high in MOFs (Ben-Mansour et al., 2016). Although a significant number of studies exist on the CO_2 separation with MOFs, acetylene separation with these new porous materials has not been thoroughly investigated and research on MOFs for acetylene separation left behind that for CO_2 separation.

Acetylene (C_2H_2) is the simplest member of unsaturated hydrocarbons and it is produced by different processes such as reaction of water with calcium carbide from coal, partial oxidation of natural gas, or as a byproduct of ethylene steam cracking (Zhang et al., 2011). C_2H_2 is a very important raw material for the synthesis of various industrial chemicals such as polyurethane and polyester plastics, consumer products, and oxy-acetylene welding and cutting in metal fabrication. Since high purity C_2H_2 is strongly needed for these processes, C_2H_2 separation is important in the industry. C_2H_2 is traditionally separated from CO_2 and CH_4 using cryogenic distillation, however this process is very costly. C_2H_2/CO_2 separation is specifically challenging because both gas molecules have similar molecular sizes ($3.4 \times 3.4 \times 5.5$ and $3.4 \times 3.4 \times 5.3$ Å) and boiling points (189.3 and 194.7 K) (Foo et al., 2016). The energy and equipment costs associated with these gas separations could be significantly reduced by the development of alternative separation methods such as adsorption-based gas separations which provide very large reductions in energy consumption and costs of these processes. The greatest limitation in the applications of adsorption-based gas separation technologies is the low selectivity of the materials used as adsorbents. Therefore, identification of new adsorbent materials that can achieve C_2H_2 separation from other gases with high selectivity has gained significant attention.

An ideal adsorbent material should offer a good combination of high adsorption selectivity and high uptake capacity in addition to good stability. There is a wide range for C_2H_2 uptake capacities of MOFs from 25 to 200 cm^3/g reported at 1 bar and 298 K (Zhang et al., 2011). Recent studies on MOFs showed that it is difficult to simultaneously achieve both high C_2H_2/CO_2 selectivity and high C_2H_2 uptake capacity (Wen et al., 2016). For example, a widely studied MOF, HKUST-1 (also known as CuBTC in the MOF literature) was reported to exhibit high C_2H_2 uptake, 201 cm^3/g at 1 bar and 298 K (Xiang et al., 2009). However, its C_2H_2/CO_2 selectivity was found to be low, 6, based on the ideal adsorbed solution theory (IAST) calculations (Myers, 2002) for equimolar C_2H_2/CO_2 mixture (Li et al., 2014). A MOF named as UTSA-50 was shown to exhibit higher C_2H_2/CO_2 selectivity, 13.3 at 1 bar and 296 K based on the Henry's law ratios of C_2H_2 and CO_2 but its C_2H_2 uptake was low, 91 cm^3/g, which was attributed to its low surface area (Xu et al., 2013). Wen et al. (2016) synthesized a new MOF and measured its C_2H_2 uptake as 216 cm^3/g at 1 bar and 298 K, which was one of the highest C_2H_2 uptakes of MOFs reported to date. They also calculated the C_2H_2/CO_2 selectivity of the MOF using IAST based on the single-component adsorption isotherms data of C_2H_2 and CO_2. Results showed that C_2H_2 selectivity is 11.5 at 1 bar for separation of an equimolar C_2H_2/CO_2 mixture. Li et al. (2014) studied C_2H_2/CO_2 separation performance of hydrogen bonded organic frameworks (HOFs) and calculated selectivity of HOF-3 using IAST as 21 at 1 bar and 296 K. Isostructural MOF-74 materials having different metal sites were reported to have high C_2H_2 uptakes, 120–197 cm^3/g at 1 bar and 295 K, however their C_2H_2/CO_2 selectivities were not reported. Xiang et al. (2010) studied the effect of metal sites on C_2H_2 storage performance of four isostructural MOFs and reported the highest C_2H_2 uptake capacity as 198 cm^3/g. Similar to C_2H_2/CO_2 separation, C_2H_2/CH_4 separation is an important process because C_2H_2 is mainly derived from the cracking of crude oil and residual oils. Purification is necessary to meet the requirement of high-purity C_2H_2 for the organic synthesis (Zhang et al., 2011). Separation of C_2H_2 from CH_4 using MOFs has been very rarely studied in the literature. UTSA-50 was reported to have a high C_2H_2/CH_4 selectivity, 68, based on the ratio of Henry's constants of gases (Xu et al., 2013).

As can be seen from this literature review, most experiments only reported the C_2H_2 uptake of MOFs and estimated MOFs' selectivities using the single-component data without performing the adsorption measurements for gas mixtures. In reality, gases exist as mixtures and selectivities should be calculated for gas mixtures. Considering the large number and variety of available MOFs, it is very challenging to identify the most promising MOF materials for adsorption-based separation of C_2H_2/CO_2 and C_2H_2/CH_4 mixtures using purely experimental manners. Molecular simulations play an important role in studying adsorption of various gas molecules in a large number of MOFs in a time effective manner to identify the best materials for a target gas separation (Colón and Snurr, 2014). There are some computational studies on C_2H_2 storage performance of MOFs in the literature (Pang et al., 2015; Chen et al., 2016; Zhang et al., 2017) however, the number of molecular simulation studies on C_2H_2 separation is very limited. Fischer et al. (2010) performed the first molecular simulation study to obtain adsorption isotherm of equimolar C_2H_2/CO_2 mixture in HKUST-1. The C_2H_2/CO_2 selectivity was calculated from the mixture data as 2.4, which was much lower than the one calculated from the single-component adsorption data (6). Yeganegi et al. (2017) carried out Grand Canonical Monte Carlo (GCMC) simulations for adsorption of equimolar C_2H_2/CH_4 mixture in MOF-5, MOF-505, and HKUST-1. The C_2H_2/CH_4 selectivity of HKUST-1 (66) was computed to be significantly higher than that of MOF-505 (6) and MOF-5 (2) at 1 bar and 295 K. Ji et al. (2017) recently performed GCMC simulations to calculate adsorption isotherms for single-component C_2H_2, CO_2, CH_4, and equimolar C_2H_2/CO_2 and C_2H_2/CH_4 mixtures at 298 K. They considered 11 MOFs having the same metal and showed that all MOFs except MOF-505 have C_2H_2/CH_4 selectivities lower than 7 and C_2H_2/CO_2 selectivities lower than 2. Selectivity of MOF-505 for C_2H_2/CH_4 was computed to be around 9 whereas selectivity for C_2H_2/CO_2 was found to be <2 at 1 bar. As can be seen from this review, current molecular simulation studies calculated C_2H_2 selectivities of at most 11 different MOF structures having the same metal.

There is no large-scale computational screening study to assess C_2H_2/CO_2 and C_2H_2/CH_4 selectivities of MOFs that span a large variety in structural properties. It is also important to note that although selectivity is a widely used metric to assess the gas separation performances of adsorbents, several other metrics such as working capacity and regenerability determine the practical usability of MOF adsorbents in separation processes. These metrics have not been examined for adsorption-based C_2H_2 separation performances of MOFs to date.

In this work, we performed molecular simulations for a large number and variety of MOFs to examine their separation potentials for C_2H_2/CO_2 and C_2H_2/CH_4 mixtures. Adsorption data of C_2H_2/CO_2 and C_2H_2/CH_4 mixtures obtained from the GCMC simulations were used to calculate several adsorbent performance metrics of MOFs including adsorption selectivity, working capacity, adsorbent performance score (APS), sorbent selection parameter and regenerability. Separation performances of MOFs were evaluated based on these metrics and the top performing MOF adsorbents were identified for C_2H_2/CO_2 and C_2H_2/CH_4 separations. We then examined the relations between structural properties of MOFs such as pore sizes, porosities, surface areas and their C_2H_2 selectivities to provide the structure-performance relationships that can serve as a map for experimental synthesis of new MOFs with better C_2H_2 separation performances.

MATERIALS AND METHODS

MOFs

We used the MOFs that represent a large variety in structure and chemistry from our previous work (Sumer and Keskin, 2016) and the crystallographic information of these MOFs were obtained from the literature (Chung et al., 2014). We also included some newly synthesized MOFs for which experimental C_2H_2 uptakes were reported and crystallographic information of these MOFs were taken from the Cambridge Structural Database (CSD) (Groom and Allen, 2014). As a result, we considered 174 different MOF structures in this work. Structural properties of MOFs such as pore limiting diameter (PLD), the largest cavity diameter (LCD), accessible surface area, pore volume and density were calculated using Zeo++ software (Willems et al., 2012). We only considered MOFs with LCDs larger than 4 Å so that all three gas molecules can be adsorbed in the pores of materials. The PLDs, LCDs, surface areas, pore volumes, and densities of MOFs range from 2.5 to 15.6 Å, 4.1 to 28.7 Å, 103 to 5,800 m^2/g, 0.08 to 3.3 cm^3/g, and 0.18 to 5.05 g/cm^3, respectively. The complete list of the MOFs studied in this work and their calculated structural properties are given in Table S1.

Simulation Details

We performed GCMC simulations to compute adsorption isotherms of gas mixtures in MOFs (Frenkel and Smit, 2002). These simulations were carried out as implemented in the RASPA simulation code (Dubbeldam, 2014). Five different types of moves, translation, reinsertion, rotation, swap, and identity exchange of molecules were considered. The Lorentz-Berthelot mixing rules were employed. The cut-off distance for truncation of the intermolecular interactions was set to 12.5 Å. The simulation cell lengths were increased to at least 25 Å along each dimension and periodic boundary conditions were applied in all simulations. For each MOF, simulations were carried out for 60,000 cycles with the first 10,000 cycles for initialization. Figure S1 shows that molecular simulation reached equilibrium at 10,000 cycles and increasing the cycle number does not affect the number of adsorbed gas molecules. Peng-Robinson equation of state was used to convert the pressure to the corresponding fugacity. More details of these simulations can be found in the literature (Frenkel and Smit, 2002; Dubbeldam, 2014).

C_2H_2 molecule was represented as a two-site rigid and linear model with the Lennard-Jones (LJ) positions located on the carbon atoms and partial charges located on each atom (Fischer et al., 2010). Unsaturated C=C and C–H bond lengths were considered as 1.211 and 1.071 Å, respectively. CO_2 molecule was modeled as a linear molecule with three LJ sites and partial charges were centered on each atom (Potoff and Siepmann, 2001). The rigid C–O bond length used in this model was 1.16 Å. Single-site spherical LJ 12–6 potential was used to model CH_4 molecules (Chen and Siepmann, 1999). All LJ parameters and atomic partial charges of gas molecules are given in Table S2.

The potential parameters of MOF atoms were taken from the Universal Force Field (UFF) (Rappé et al., 1992) since UFF has been successful in predicting gas adsorption and separation performances of a large number of MOFs in previous studies (Keskin et al., 2009). Furthermore, UFF contains potential parameters for all elements of the periodic table and applicable to all types of MOFs having a variety of atoms. Potential parameters of Cu atoms of MOFs were taken from a molecular simulation study (Fischer et al., 2010) in which modified parameters for Cu was shown to better represent the interaction of carbon site of C_2H_2 and oxygen site of CO_2 with the unsaturated Cu sites of MOFs. Electrostatic interactions were taken into account using the Coulomb potential. In order to compute the electrostatic interactions between gas molecules and MOFs, partial point charges were assigned to MOF atoms using the extended charge equilibration method (EQeq; Wilmer et al., 2012). MOFs were assumed to be rigid in their reported crystallographic structures in the simulations. This assumption has been used in all large-scale molecular simulation studies of MOFs to save significant computational time. Since we only considered the MOFs that have pore sizes larger than the kinetic diameters of the gas molecules, flexibility is expected to have a negligible effect on the gas adsorption results. All GCMC simulations were performed at an adsorption pressure of 1 bar and desorption pressure of 0.1 bar at 298 K since the compression limit for the safe storage of C_2H_2 is 2 bar. These conditions were chosen to mimic vacuum swing adsorption process following the literature (Bae and Snurr, 2011). Equimolar C_2H_2/CO_2 and C_2H_2/CH_4 mixtures were considered in all molecular simulations. It was recently discussed that the two most important factors in molecular simulations are the force field and the degree of sampling in the relevant configuration space (van Gunsteren et al., 2017). In order to show the good sampling of our simulations, we reported the deviations of GCMC results for the top three promising MOFs for C_2H_2/CO_2

and C_2H_2/CH_4 separations in Table S3 and results showed that the uncertainty for the simulated C_2H_2 adsorption is <3%.

Adsorbent Evaluation Metrics

Results obtained from GCMC simulations were used to compute several adsorbent evaluation metrics that are defined in **Table 1**. Adsorption selectivity (S_{ads}) is the most widely used metric to evaluate adsorbents and it is simply defined as the ratio of compositions of the adsorbed gases (x) in the adsorbent normalized by the ratio of bulk phase compositions (y). The subscript 1 represents the strongly adsorbed gas and subscript 2 represents the weakly adsorbed gas. Since the aim of our work is to identify the MOFs that are able to selectively separate C_2H_2 from CO_2 and CH_4, we reported C_2H_2/CO_2 and C_2H_2/CH_4 selectivities of MOFs. Working capacity (ΔN) is defined as the difference between the gas uptakes (N) at the adsorption and desorption pressures in the unit of mol gas per kg adsorbent (Bae and Snurr, 2011). We computed C_2H_2 working capacity of all MOFs. APS was defined as the product of selectivity and working capacity to easily identify the top performing adsorbent materials that combine high selectivities with high working capacities (Chung et al., 2016). Sorbent selection parameter (S_{sp}) includes the ratio of working capacities and selectivities computed at adsorption and desorption pressures and it is useful for studying the performance of adsorbents in pressure swing adsorption processes (PSA; Rege and Yang, 2001). Per cent regenerability (R%) describes the regeneration of the adsorption sites and shows the reusability of the adsorbent in the cyclic processes (Bae and Snurr, 2011).

RESULTS AND DISCUSSIONS

The accuracy of our GCMC simulations to assess the adsorption of CO_2 and CH_4 molecules in various MOFs was validated in our previous works (Sezginel et al., 2015; Altintas and Keskin, 2016; Sumer and Keskin, 2016) by comparing the results of our molecular simulations with the available experimental data from different research groups. In this work, we aim to validate the GCMC simulations for C_2H_2 adsorption in MOFs. We collected experimental C_2H_2 uptake data of several different MOFs from the literature and performed GCMC simulations for these MOFs under the same conditions with the experiments at 1 bar and 298 K (in some cases 296 K). We specifically included the widely studied MOFs such as MOF-5 (IRMOF-1), HKUST-1, ZIF-8, UTSA-50 and the MOFs identified as promising due to their high C_2H_2 uptakes such as Co-DHTP in this comparison. **Figure 1** shows that there is a good agreement between single-component adsorption experiments and simulations for C_2H_2 uptakes of different MOFs, indicating the appropriate choice of the force fields used in the simulations. The good agreement between experimentally reported and simulated C_2H_2 adsorption isotherms of IRMOF-1 and HKUST-1 up to 1 bar is also shown in Figure S2. There was no experimental data on adsorption of equimolar C_2H_2/CO_2 and C_2H_2/CH_4 mixtures in the literature to the best of our knowledge, therefore it was not possible to make a comparison for the mixture adsorption. The good agreement we showed in **Figure 1** suggests that molecular simulations can be used to make accurate estimates about the adsorption of C_2H_2/CO_2 and C_2H_2/CH_4 mixtures in MOFs.

TABLE 1 | Descriptions of adsorbent evaluation metrics.

Metric	Equation
Selectivity	$S_{ads(1/2)} = \frac{x_1/x_2}{y_1/y_2}$
Working capacity	$\Delta N = N_{ads} - N_{des}$
Adsorbent performance score	$APS = S_{ads} \times \Delta N$
Sorbent selection parameter	$S_{sp} = \frac{{S_{ads,1}}^2}{S_{des,1}} \times \frac{\Delta N_1}{\Delta N_2}$
Regenerability	$R(\%) = \frac{\Delta N}{N_{ads}} \times 100\%$

We performed the GCMC simulations of MOFs at 0.1 and 1 bar considering equimolar C_2H_2/CO_2 and C_2H_2/CH_4 mixtures and computed their C_2H_2 selectivities and working capacities. All 174 MOFs were found to be C_2H_2 selective for C_2H_2/CH_4 separation whereas 121 MOFs were found to be C_2H_2 selective for C_2H_2/CO_2 separation. Since our aim is to identify C_2H_2 selective MOFs in this work, we only show these 121 MOFs in **Figure 2A**. **Figure 2A** shows that most of the MOFs have C_2H_2/CO_2 selectivities lower than 2. These low selectivities can be attributed to the similarity of the C_2H_2 and CO_2 molecules which makes the adsorption-based C_2H_2/CO_2 separation challenging. There are 25 MOFs that show C_2H_2/CO_2 selectivities in the range of 2–10 and widely studied HKUST-1 is among these MOFs. We calculated its selectivity as 2.9 which is in good agreement with the literature value of 2.4 (Fischer et al., 2010). This slight difference can be attributed to (a) the different potential parameters used for CO_2, (b) the different charge assignment methods used for CuBTC and/or (c) different crystal structures of CuBTC used in two simulation studies. Three MOFs, UWUTIQ, CUVTUJ

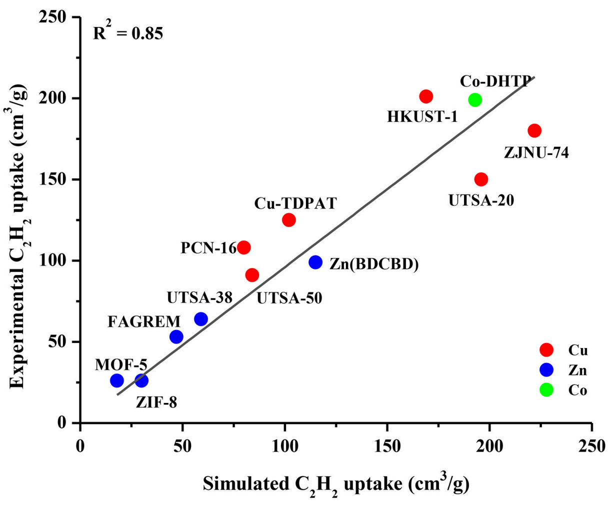

FIGURE 1 | Comparison of experimental and simulated C_2H_2 uptakes of MOFs at 1 bar, 298 K.

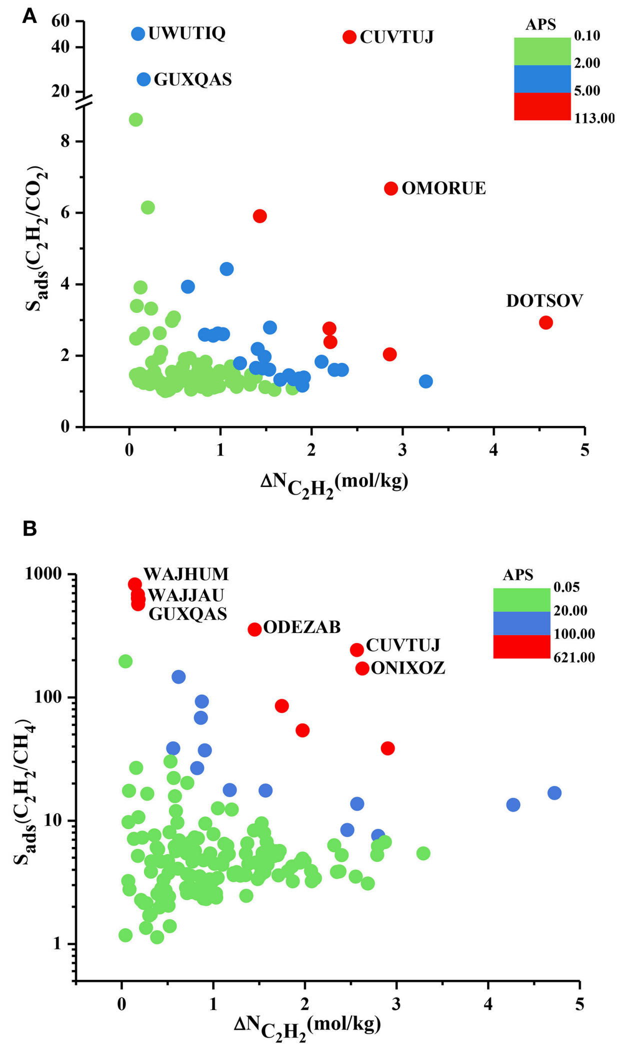

FIGURE 2 | C_2H_2 selectivity and C_2H_2 working capacity of MOFs for separation of equimolar **(A)** C_2H_2/CO_2 **(B)** C_2H_2/CH_4 mixtures.

[also known as Co_2(DHTP)] and GUXQAS, were found to show the highest C_2H_2/CO_2 selectivities of 49, 47, and 24, respectively. The highest C_2H_2/CO_2 selectivities were reported for UTSA-50 and HOF-3 using IAST calculations as 13 and 21, respectively (Xu et al., 2013; Li et al., 2014). The three MOFs mentioned above outperform UTSA-50 and HOF-3 in terms of selectivity. On the other hand, **Figure 2A** shows that MOFs with high C_2H_2/CO_2 selectivities generally suffer from low C_2H_2 working capacities. A large number of MOFs was found to exhibit C_2H_2 working capacities lower than 2 mol/kg. The best MOF adsorbents are expected to offer both high C_2H_2 selectivities and high C_2H_2 working capacities. In order to identify the MOFs that offer a good combination of C_2H_2 selectivity and C_2H_2 working capacity, we color-coded **Figure 2A** with APS values to separate low and high-performance regions within the MOF search space. Three different regions were defined to provide a reference for quantitatively identifying a number of promising MOFs. MOFs with high C_2H_2 selectivity but low C_2H_2 working capacity and MOFs with low C_2H_2 selectivity but high C_2H_2 working capacity were located in the green region. These MOFs have APS values lower than 2 for separation of equimolar C_2H_2/CO_2 mixtures. MOFs showing moderate selectivities (1.2–49) and working capacities (0.1–3.25 mol/kg) result in APS values of 2.14–4.76 and they are shown in the blue region. Finally, the most promising MOFs with the best selectivity and working capacity combinations are shown in the red region with APS $>$ 5.25. There are 7 MOFs in this region and except one all have C_2H_2/CO_2 selectivities in the range of 2–7 and their working capacities are between 1.5 and 3 mol/kg. Three MOFs with the highest APSs, CUVTUJ, OMORUE, and DOTSOV can be considered as the best candidates for C_2H_2/CO_2 separations.

Figure 2B shows that C_2H_2/CH_4 selectivities of MOFs have a wide range from 1.2 to 824, and most of the MOF adsorbents have C_2H_2 selectivities lower than 10. The C_2H_2 working capacities of MOFs were also calculated to span a wide range, from 0.04 to 4.7 mol/kg. For equimolar C_2H_2/CH_4 mixture, Alduhaish et al. (2017) reported the highest selectivity, 98, for a MOF (VAQXUJ) using IAST at 1 bar and 296 K. Ten MOFs we studied exhibit higher selectivities than this record. The top three selective MOFs were identified to be WAJHUM, WAJJAU, GUXQAS with C_2H_2/CH_4 selectivities of 824, 684, 638, respectively. These MOFs outperform the widely studied MOFs such as HKUST-1 and UTSA-50 which were reported to have C_2H_2/CH_4 selectivities of ∼66–68 at 1 bar, 295/296 K as we discussed above. The four MOFs with the highest selectivities suffer from low C_2H_2 working capacities, ∼0.17 mol/kg. The combination of high selectivity and low working capacity of these MOFs can be attributed to their relatively low pore volumes ($<$0.45 cm^3/g). CUVTUJ and ONIXOZ exhibit both high C_2H_2/CH_4 selectivities (242 and 171, respectively) and high C_2H_2 working capacities (∼2.6 mol/kg). Similar to **Figure 2A**, we color-coded the APSs of MOFs where green represents the MOFs with low performance (APSs $<$ 20), blue represents the promising MOFs with C_2H_2/CH_4 selectivities of 7.5–147, C_2H_2 working capacities of 0.6–5 mol/kg, resulting in 20 $<$ APSs $<$ 92. Finally, the most promising MOFs for separation of equimolar C_2H_2/CH_4 mixtures are located in the red region with APSs $>$ 102. The best candidates for C_2H_2/CH_4 separations were identified as CUVTUJ, ONIXOZ (high selectivity and high working capacity), and ODEZAB (high selectivity and moderate working capacity). These MOFs were computed to have APSs of 621, 450, and 515, respectively.

At that point it is also useful to compare the C_2H_2 working capacities of MOFs with each other. Zhang et al. (2017) calculated single-component C_2H_2 working capacities of 7 MOF structures as 110–180 cm^3 (STP)/g at an adsorption pressure of 1 bar and desorption pressure of 0.1 bar. The highest C_2H_2 working capacities of the 174 MOFs we considered in this work were calculated to be as 103 cm^3 (STP)/g and 106 cm^3 (STP)/g for C_2H_2/CO_2 and C_2H_2/CH_4, respectively, under the same conditions. These values belong to a well-known MOF, HKUST-1. It is important to note that our C_2H_2 working capacities were calculated for equimolar mixtures, not for the single-component gas adsorption and therefore they are less than the ones reported for single-component cases.

We showed the S_{sp} values of MOFs for separation of C_2H_2/CO_2 and C_2H_2/CH_4 mixtures in **Figure 3** as a function of selectivity. S_{sp} values of MOF adsorbents are in the range of 0.1–755 and 1.2–101,362 for C_2H_2/CO_2 and C_2H_2/CH_4 separations, respectively. S_{sp} increases with selectivity as described in **Table 1**. Most of the MOFs have S_{sp} values lower than 10 for C_2H_2/CO_2 separation due to the low selectivities as shown in **Figure 3A**. S_{sp} values of MOFs are <100 for C_2H_2/CH_4 separation as shown in **Figure 3B**. It is important to note that a MOF which has been widely studied as adsorbent in the literature, IRMOF-1 (SAHYIK), has a low S_{sp} (3.1) for C_2H_2/CH_4 separation. This means there are many other MOFs with better separation potentials than this widely studied MOF. The most promising MOFs are located at the top right corner of **Figure 3** which have both high S_{sp} and high selectivity such as UWUTIQ (S_{sp}: 754.88, S_{ads}:49) for C_2H_2/CO_2 and WAJHUM for C_2H_2/CH_4 (S_{sp}: 101,36 and S_{ads}: 824). To summarize, APS identifies CUVTUJ, OMORUE, and DOTSOV (CUVTUJ, ODEZAB, and ONIXOZ) as the best adsorbents for C_2H_2/CO_2 (C_2H_2/CH_4) separation whereas S_{sp} identifies UWUTIQ, CUVTUJ, and OMORUE (WAJHUM, WAJJAU, and WAJJEY) as the best adsorbents for C_2H_2/CO_2 (C_2H_2/CH_4) separation. These results show that for C_2H_2/CO_2, CUVTUJ, and OMORUE are the promising adsorbents based on both APS and S_{sp}. The low working capacity of UWUTIQ, which has the highest selectivity and S_{sp}, leads to a low APS value. MOFs that are promising for separation of C_2H_2/CH_4 were identified to be different based on these two metrics because MOFs with high selectivities generally have low working capacities (as shown in **Figure 2B**) resulting in high S_{sp} but low APS values.

Figure 4 shows the relation between R% and selectivity of MOFs. MOFs show a very wide range of R%, from 2 to 91% for these two mixtures and the red dotted line represents R% = 80%. We chose this value as the minimum desired R% since lower R% values result in high cost in adsorption-based gas separation applications (Li et al., 2009). There is generally an inverse relation

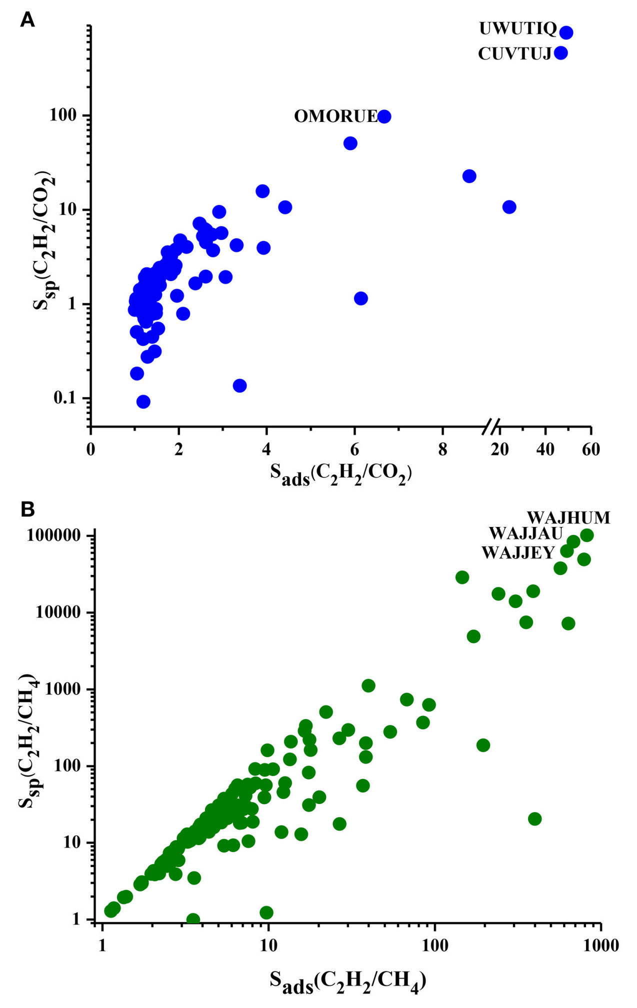

FIGURE 3 | S_{sp} and S_{ads} of MOFs for **(A)** C_2H_2/CO_2 and **(B)** C_2H_2/CH_4 separations.

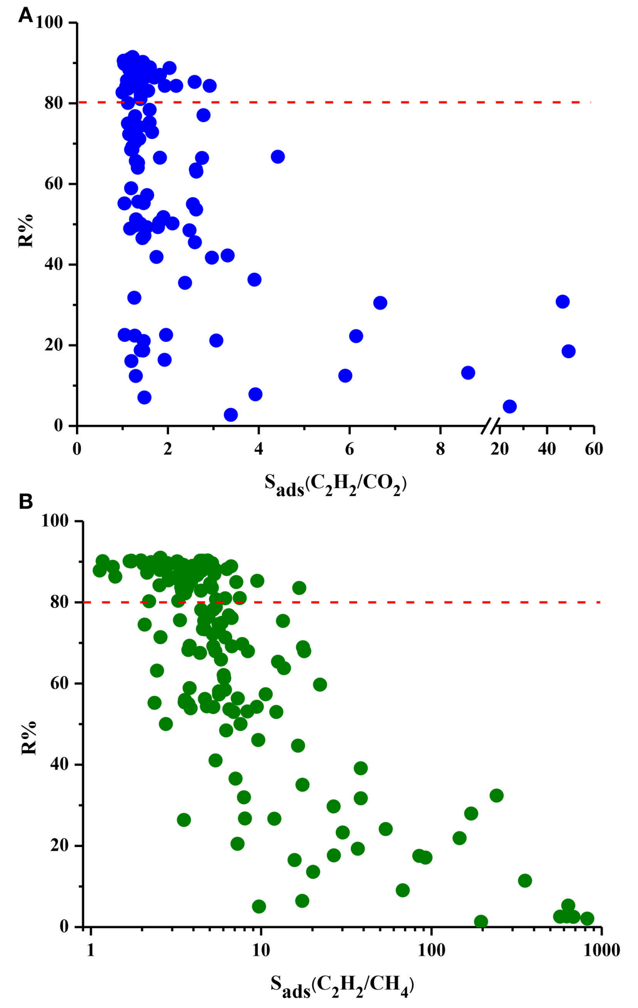

FIGURE 4 | R% and S_{ads} of MOFs for **(A)** C_2H_2/CO_2 and **(B)** C_2H_2/CH_4 mixtures.

between R% and S_{ads}. As the MOF strongly adsorbs one gas component over other, desorption becomes difficult resulting in low working capacities and low regenerabilities. Almost half of the MOFs exhibit R% higher than 80%, however these MOFs have low selectivities. For example, the three most selective MOFs for C_2H_2/CO_2 separation have very low R% values of 18, 31, and 5% as can be seen from **Figure 4A.** Similarly, three MOFs with the highest C_2H_2/CH_4 selectivities suffer from very low R% (2, 3, and 5%, respectively) as shown in **Figure 4B**. These results show that choosing the best adsorbent material based on solely selectivity is not completely accurate and other metrics such as R% should be considered. Among the MOFs which have R% higher than 80%, DOTSOV shows the highest selectivity of 3 and 17 for C_2H_2/CO_2 and C_2H_2/CH_4 mixtures, respectively. This MOF also exhibits high C_2H_2 working capacity for C_2H_2/CO_2 and C_2H_2/CH_4 (4.6 and 4.73 mol/kg) suggesting that it is a promising adsorbent for both separations considering the cost of regeneration.

Understanding the correlations between separation performances of MOF adsorbents and their structural properties is crucial for identification of the best candidates with pre-determined structural features. Since selectivity is the most widely considered metric in choosing adsorbents, we examined the relation between LCDs of MOFs and their selectivities in **Figure 5**. Results show that MOFs having pores in the range of 5–10 Å generally have high selectivities both for C_2H_2/CO_2 and C_2H_2/CH_4 separations whereas MOFs with LCDs > 10 Å exhibit low adsorption selectivities. This result is in agreement with the findings of a recent study in which MOFs with LCDs of 6.7–10 Å were found to have the highest single-component C_2H_2 uptakes (Zhang et al., 2017). **Figure 6** shows the relation between accessible surface areas of MOFs and their selectivities. MOFs having surface areas between 180 and 1,200 m^2/g have higher C_2H_2/CO_2 selectivities whereas MOFs with surface areas of 550–1,800 m^2/g are more promising for selective separation of C_2H_2 from CH_4. Although there is not a very strong relation between surface area and selectivity, **Figure 6B** suggests that MOFs with large surface areas (>3,500 m^2/g) are not very selective. We also investigated the relation between APSs and accessible surface areas of MOFs in Figure S3. Similar to selectivity, there is not an obvious relation but MOFs having high APSs generally have surface areas of 1,100–3,200 and 1,000–2,300 m^2/g for C_2H_2/CO_2 and C_2H_2/CH_4 separations, respectively. No obvious relation was found between selectivity, APS and porosity of MOFs as shown in Figures S4, S5 but lower porosities generally lead to higher selectivities. As a result, we concluded that pore sizes smaller than 10 Å, surface areas <2,000 m^2/g and low porosities (0.41–0.64) provide a stronger confinement for the C_2H_2 molecules compared to CO_2 and CH_4 and lead to higher C_2H_2 selectivities. At that point, it is important to note that selectivity of a material is determined by the interplay of various factors and cannot be easily correlated to only a few structural properties as we attempted to do. For example, chemical composition and topology of MOFs strongly affect the affinity of materials for specific gas molecules but these correlations are very complex and they can be only captured if a very large number and variety of structures are investigated. The simple correlations that we demonstrated in **Figures 5**, **6** will provide useful information to accelerate the design of new high-performance MOFs for C_2H_2 separation applications.

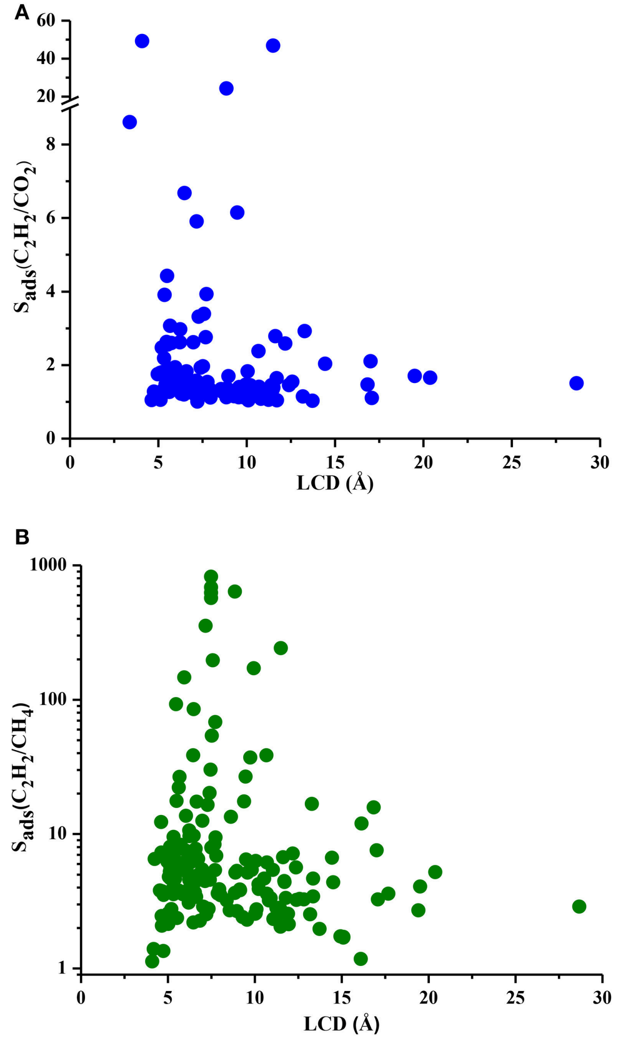

FIGURE 5 | S_{ads} and LCD of MOFs for **(A)** C_2H_2/CO_2 and **(B)** C_2H_2/CH_4 mixtures.

We finally investigated the effect of composition of the gas mixture on the separation performance of the MOFs. CUVTUJ and GUXQAS are the promising MOFs for C_2H_2/CO_2 and C_2H_2/CH_4 separations due to their high selectivities and high APSs. Outstanding performance of these two MOFs motivated us to investigate their separation performance for mixtures with different compositions. We performed GCMC simulation for these two MOFs at 1 bar, 298 K by changing the C_2H_2 mole fraction (y_{C2H2}) in the bulk mixture. **Figure 7A** shows that as y_{C2H2} increases, selectivities of CUVTUJ and GUXQAS decrease. There are sharp decreases in the selectivities of both MOFs with increasing y_{C2H2} from 0.1 to 0.5. In this region, increasing y_{C2H2} results in an increase in the adsorbed C_2H_2 (x_{C2H2}) and decrease in the adsorbed CO_2 (x_{CO2}). Since the selectivity was

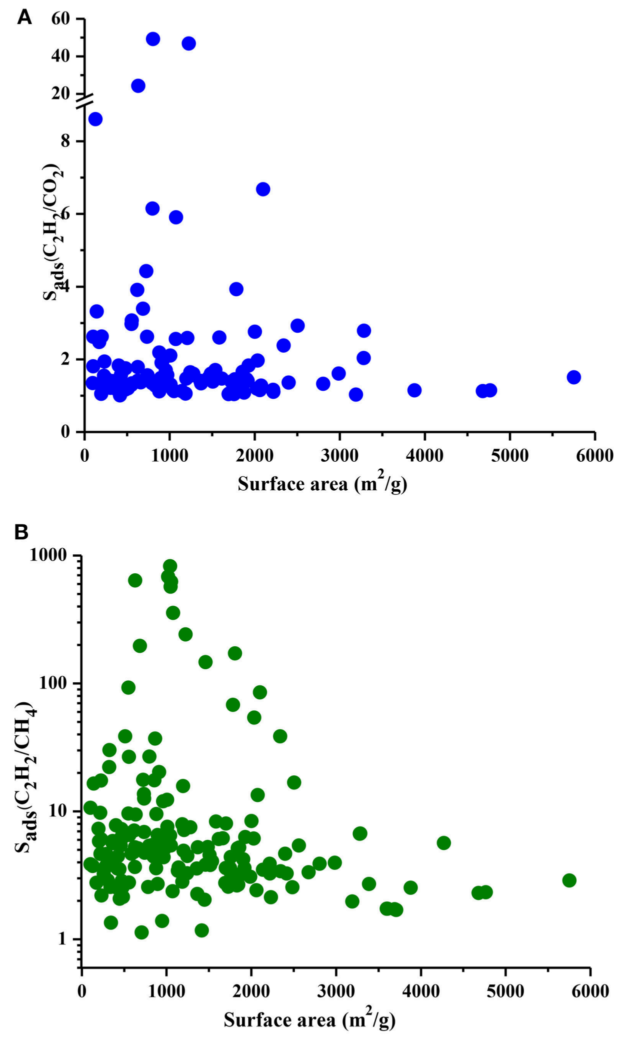

FIGURE 6 | S_{ads} and surface areas of MOFs for **(A)** C_2H_2/CO_2 and **(B)** C_2H_2/CH_4 mixtures.

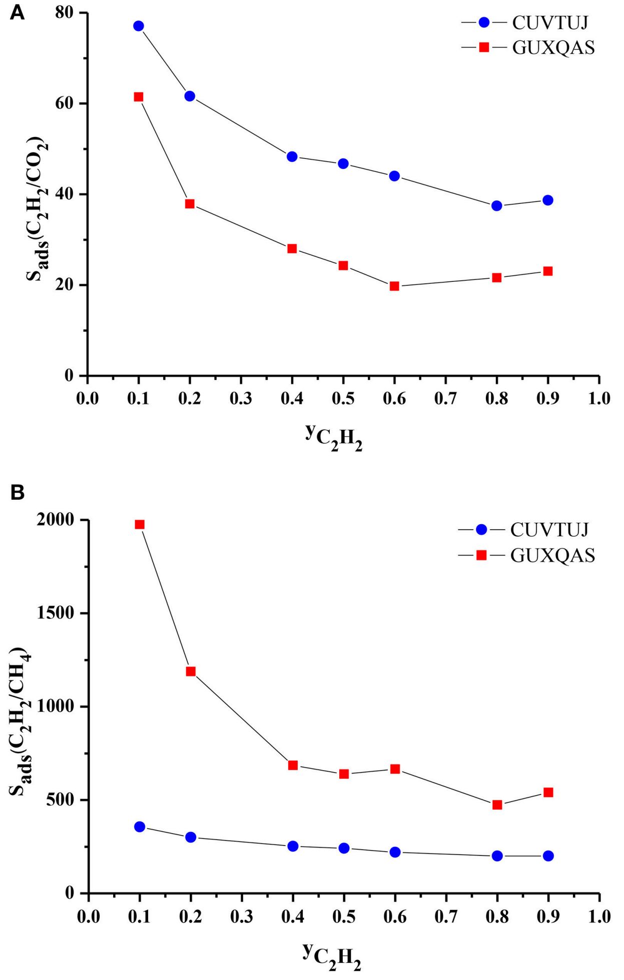

FIGURE 7 | (A) C_2H_2/CO_2 and **(B)** C_2H_2/CH_4 selectivity of promising MOFs as a function of C_2H_2 composition in the bulk mixtures.

normalized by the bulk composition, C_2H_2/CO_2 selectivities decrease with y_{C2H2}. **Figure 7B** shows that GUXQAS has a very high C_2H_2/CH_4 selectivity for mixtures with $y_{C2H2} < 0.5$. x_{C2H2} of GUXQAS does not change remarkably by increasing y_{C2H2}, however x_{CH4} decreases resulting in sharp reductions in the C_2H_2/CH_4 selectivities. The selectivity of CUVTUJ does not have a very significant dependence on the y_{C2H2} as can be seen from **Figure 7B**.

Finally, it is important to discuss the effect of force field selection on the results of molecular simulations. Generic force fields were found to be less successful in predicting gas adsorption in materials having strong binding sites, such as open metal sites (Getman et al., 2012). Specific force fields derived from quantum chemical calculations are required to describe the interactions between gas molecules and MOFs having open metal sites. The key challenge in developing such force fields using quantum chemistry calculations is selecting the appropriate level of theory and balancing it with the computational expense. There may be several MOFs having open metal sites and showing strong binding for C_2H_2 molecules but we did not define a specific force field for them and screened the MOFs using generic force fields. The value of our calculations is to efficiently identify the most promising MOF materials using generic, off-the-shelf-force fields, in a time-efficient manner. More detailed quantum chemistry calculations can be further performed for the best candidates to understand the underlying mechanism in future studies.

Our molecular simulations give no information about stability of MOFs, however an adsorbent should be stable in order to find place in practical applications. Therefore, we collected the stability information of the top three promising MOFs from their experimental synthesis articles. There is no specific stability information in the literature for CUVTUJ, OMORUE, and ONIXOZ. DOTSOV was reported to be thermally stable up to 240°C (Wu et al., 2008), UMUTIQ (Das et al., 2011) and GUXQAS (Ling et al., 2009) were reported to save their stabilities up to high temperatures. WAJHUM and WAJJAU were reported in the same experimental work and their thermal stabilities were investigated in detail (Xie et al., 2010). ODEZAB was reported to be thermally stable up to around 300°C after evacuating solvent molecules from its structure (Duan et al., 2016). Stabilities of the most promising materials identified in this work are most likely to be examined under practical gas separation experiments in future studies.

CONCLUSIONS

Developing effective adsorbents for challenging separations of C_2H_2/CO_2 and C_2H_2/CH_4 is crucial in order to meet the requirement of high purity C_2H_2 in various industries. MOFs are strong candidates for storage of C_2H_2, but limited information was available about their C_2H_2 separation potentials. We performed the first large-scale molecular simulation study to examine the potential of 174 different MOF structures for separation of C_2H_2/CO_2 and C_2H_2/CH_4 mixtures. Several MOFs were identified to show high C_2H_2 selectivities. The top three most promising MOF adsorbents were computed to have C_2H_2/CO_2 selectivities of 49, 47, 24, and C_2H_2/CH_4 selectivities of 824, 684, 638 at 1 bar, 298 K. These are the highest C_2H_2 selectivities reported to date in the literature. Two MOFs, CUVTUJ and GUXQAS, were found to be very promising both for C_2H_2/CO_2 and C_2H_2/CH_4 separations leading to selectivities of 47 (242) and 24 (638), respectively. In addition to selectivity, other adsorbent evaluation metrics such as APS, $S_{sp,}$ R% were computed for all MOFs. Results showed that highly selective MOFs suffer from low R% and therefore choosing the best adsorbent material based on solely selectivity is not completely accurate. We also examined the structure-performance relations of MOFs and showed that MOFs with pore sizes <10 Å, surface areas <2,000 m^2/g and low porosities (0.41–0.64) lead to higher C_2H_2 selectivities. We believe that these results will motivate extensive research on MOF adsorbents for C_2H_2 separation processes.

AUTHOR CONTRIBUTIONS

AN: performed the molecular simulations and contributed to writing of the manuscript; SK: discussed the results and wrote the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2018.00036/full#supplementary-material

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