Storage and Separation of CO₂ and CH₄ in Silicalite, C₁₆₈ Schwarzite, and IRMOF-1: A Comparative Study from Monte Carlo Simulation

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Received August 3, 2006. In Final Form: September 23, 2006

Storage of pure CO₂ and CH₄ and separation of their binary mixture in three different classes of nanostructured adsorbents—silicalite, C₁₆₈ schwarzite, and IRMOF-1—have been compared at room temperature using atomistic simulation. CH₄ is represented as a spherical Lennard-Jones molecule, and CO₂ is represented as a rigid linear molecule with a quadrupole moment. For pure component adsorption, CO₂ is preferentially adsorbed than CH₄ in all the three adsorbents over the pressure range under this study, except in C₁₆₈ schwarzite at high pressures. The simulated adsorption isotherms and isosteric heats match closely with available experimental data. A dual-site Langmuir—Freundlich equation is used to fit the isotherms satisfactorily. Compared to silicalite and C₁₆₈ schwarzite, the gravimetric adsorption capacity of pure CH₄ and CO₂ separately in IRMOF-1 is substantially larger. This implies that IRMOF-1 might be a potential storage medium for CH₄ and CO₂. For adsorption from an equimolar binary mixture, CO₂ is preferentially adsorbed in all three adsorbents. Predictions of mixture adsorption with the ideal-adsorbed solution theory on the basis of only pure component adsorption agree well with simulation results. Though IRMOF-1 has a significantly higher adsorption capacity than silicalite and C₁₆₈ schwarzite, the adsorption selectivity of CO₂ over CH₄ is found to be similar in all three adsorbents.

I. Introduction

Combustion of fossil fuels has generated a huge amount of greenhouse gas CO₂. The relationship between anthropogenic emission of CO₂ and increased temperature has been well recognized, and the effect of increasing atmospheric CO₂ concentration on global warming is now regarded as one of the most pressing environmental issues. To reduce the atmospheric level of CO₂ while minimizing the world economic impact, four strategies have been proposed: (1) carbon sequestration, (2) less carbon-intensive fuels, (3) more energy-efficient methods, and finally (4) increased conservation. It is expected that CO₂ sequestration to be implemented in the coming 30 years will be both economically and environmentally attractive, and several approaches have been developed such as chemical conversion, solvent absorption, deep-sea deposition, and adsorption in porous media. Compared to the commonly used purification technique of CO₂ absorption, adsorption is technically feasible, affordable, and energy-efficient. In the long run, use of less carbon-intensive fuels, for example, natural gas, will help in reducing overall CO₂ emissions. The major component in natural gas is CH₄, and thus it is essential to find a suitable adsorptive material for CH₄ storage. On the other hand, CO₂ is often found as a major impurity in natural gas, and its presence can reduce the energy content of natural gas. Consequently, in addition to the storage of pure CO₂ and CH₄ separately, it is also important to separate them from their mixture. By a careful selection of the adsorbent, CO₂ and CH₄ can be effectively separated on the basis of the different adsorption affinities.

Several experimental and simulation studies have been reported on the adsorption of gases in various adsorbents, and many of these have been summarized in two recent books. Using the Monte Carlo method, Yue and Yang studied the influence of temperature, pressure, and composition on the adsorption of pure and binary mixture of CO₂ and benzene in silicalite. Goj et al. simulated the adsorption of CO₂ and N₂, both as single component and as binary mixture, in three zeolites with identical chemical composition but differing pore structures. Eckhard and Matthias analyzed the adsorption of binary mixture of CH₄/CF₃ in silicalite using a gravimetric method and compared with the prediction of the ideal-adsorbed solution theory (IAST) and a multisite Langmuir model on the basis of the adsorption of single components. Sarkar and Bose used activated carbon pellets to adsorb CO₂ and CH₄, and their study showed that IRMOF-1 is a promising adsorbent for CO₂ and CH₄ separation.


10.1021/la062289p CCC: $37.00 © 2007 American Chemical Society
Published on Web 11/17/2006
study the removal of CO₂. Jiang and Sandler⁹–¹² investigated the adsorption of O₂ and N₂ in carbon nanotube bundles and of CO₂ and N₂ in C₁₆₈ schwarzite as a model for nanoporous carbon. In addition, there are a few studies of the adsorptive separation of CO₂/CH₄ mixtures in porous materials. Nicholson and Gubbins¹³ examined the effects of geometry and energetics on the selectivity from a CO₂/CH₄ mixture. Peng et al.¹⁴ measured the adsorption of pure and mixed CO₂ and CH₄ in activated mesocarbon microbeads and used an equation of state to correlate the experimental data. Vu et al.¹⁵ used carbon molecular hollow fiber membranes for CH₄/CO₂ separation at different temperatures with high pressure mixed-gas feed of 10% CO₂ and 90% CH₄.

The selection of a suitable adsorbent is a key step in the design of adsorption-based storage or separation processes. As mentioned above, most studies have focused on zeolites and carbon-based adsorbents. Recently, a new class of porous materials has been developed, the metal organic frameworks (MOFs), which consist of metal–oxide clusters and organic linkers.¹⁶–¹⁸ Inorganic porous materials, such as zeolites in which the Si–O and Al–O bonds have tetrahedral oxide skeletons, generally can be produced in only a limited range of structures. Essentially as organic zeolites, MOFs allow the formation of flexible porous frameworks with a wide variety of architectures, topologies, and pore sizes. They provide almost unlimited opportunities to develop, control, and tune structures for specific applications.¹⁹ Because of their high porosity and well-defined pore size, MOFs are promising candidates for the storage of gases, the separation of mixtures, and ion-exchanges.²⁰

In this work, using atomistic simulation, we have investigated the storage capacity for pure CO₂ and CH₄ and the separation of their binary mixture in three different adsorbents: silicalite, C₁₆₈ schwarzite, and IRMOF-1. Each of them has a well-defined three-dimensional periodic structure with nanoscaled channels, and each represents a typical class of nanoporous material. In section II, we describe the models used for the three adsorbents and the two adsorbates. In section III, the Monte Carlo simulation method is briefly described. The adsorption isotherms of both pure and binary components, isosteric heats of adsorption, Henry constants, and simulation snapshots are presented in section IV, followed by concluding remarks in section V.

II. Models

Silicalite. Usually denoted as MFI, silicalite is an Al-free zeolite existing in three distinct crystal forms: monoclinic and Pnma and P2₁2₁2 orthorhombic structures. In this work, we consider the Pnma orthorhombic structure. The unit cell has 96 Si atoms and 192 O atoms, and the lattice constants are \( a = 20.06 \, \text{Å}, \, b = 19.80 \, \text{Å}, \) and \( c = 13.36 \, \text{Å} \). As shown in Figure 1a, MFI consists of two types of channels with 10-membered rings, one is straight and the other is zigzag (sinusoidal). These channels have diameters of approximately 5.4 Å. This implies that an adsorbate molecule with a van der Waals diameter of about 5.4 Å or less can fit inside these channels. A unit cell has two straight channels, two zigzag channels, and two channel intersections.²¹ The potential parameters of the Si and O atoms were taken from the work of Hirotani et al.,²² as listed in Table 1, which had been optimized to reproduce the experimental heats of adsorption. In most of the previous simulation studies of adsorption in zeolites, the short-ranged dispersion interaction of Si atoms was neglected because of its weak contribution, and thus only electrostatic interaction was taken into account. To model the framework full atomistically, in this work both the

dispersion and electrostatic interactions are considered for the O and Si atoms.

**C168 Schwarzite.** Nanoporous carbon membranes are amorphous and do not have well-defined structures, consequently, the hypothetical C168 schwarzite is used in this work to represent the nanoporous carbon. C168 schwarzite has a simple periodic structure with well-defined channels, and carbon-surface curvatures are similar to those in realistic samples. In addition to the primary six-membered rings, there are also five-, seven-, and eight-membered rings. The unit cell of the C168 schwarzite has a length of 21.8 Å and 672 carbon atoms. As shown in Figure 1b, there are two types of channels in C168 schwarzite with average diameters of approximately 7 and 9 Å, respectively. The channels in the same layer are isolated from each other, but they are connected with those in the neighboring layers by channel intersections. In the same layer, the channels with average diameters of approximately 7 and 9 Å, respectively. The channels in the same layer are isolated from each other, but they are connected with those in the neighboring layers by channel intersections.

**IRMOF-1.** IRMOF-1 is an isoreticular MOF and is also known as MOF-5.10 It has a lattice constant of 25.832 Å, a crystal density of 0.593 g/cm³, a free volume of 79.2%, and a surface area of 2833 m²/g.23 For simulation, the atomic coordinates within the unit cell of the C168 schwarzite has a length of 21.8 Å and 672 carbon atoms. As shown in Figure 1b, there are two types of channels in C168 schwarzite with average diameters of approximately 7 and 9 Å, respectively. The channels in the same layer are isolated from each other, but they are connected with those in the neighboring layers by channel intersections.

**Adsorbates.** CH₄ is modeled by the united-atom model, which has been demonstrated to give comparable adsorption isotherms for alkane adsorption in MFI but with less computational effort compared to the all-atom model.29 The intermolecular potential parameters of CH₄ given in Table 1 are from the TraPPE force field developed to reproduce the critical parameters and saturated liquid densities of alkanes.30 The interactions between CH₄ and adsorbent is modeled using the Lennard-Jones (LJ) potential, and the Lorentz–Berthelot mixing rules are used to calculate cross interaction parameters.

CO₂ is represented as a three-site rigid molecule. The intrinsic quadrupole moment is described by the potential model. The partial charge on the C atom is 0.576 e, and by electro-neutrality, the partial charge on O atom is −0.288 e. The CO bond length is 1.18 Å, and the bond angle OCO is 180°. The CO₂–CO₂ intermolecular interactions are modeled as a combination of LJ and Coulombic potentials with the potential parameters given in Table 1, which are very close to the elementary physical model fitted to the experimental vapor–liquid equilibrium data of bulk CO₂.32

**III. Methodology**

Grand canonical Monte Carlo (GCMC) simulations at fixed temperature T, volume V, and adsorbate chemical potential μ were carried out for the adsorption of pure CO₂ and CH₄ and their mixture in MFI, C168 schwarzite, and IRMOF-1. GCMC simulation allows one to directly relate the chemical potential in adsorbed and bulk phases, and it has been used widely for the simulation of adsorption. Unlike our previous simulation studies,10 there are two different types of O atoms and three different types of C atoms. Adsorbates. CH₄ is modeled by the united-atom model, which has been demonstrated to give comparable adsorption isotherms for alkane adsorption in MFI but with less computational effort compared to the all-atom model.29 The intermolecular potential parameters of CH₄ given in Table 1 are from the TraPPE force field developed to reproduce the critical parameters and saturated liquid densities of alkanes.30 The interactions between CH₄ and adsorbent is modeled using the Lennard-Jones (LJ) potential, and the Lorentz–Berthelot mixing rules are used to calculate cross interaction parameters.
Robinson equation of state (PR EOS). For CO₂/CH₄ mixture, the binary interaction parameter in the PR EOS was simply assumed to be zero.

The simulation box representing MFI contained 12 (2 × 2 × 3) unit cells, while for C₁₆₈ schwarzite and IRMOF-1 8 (2 × 2 × 2) unit cells were used. No finite-size effect was found in larger simulation box. All the three adsorbents were treated as rigid with atoms frozen during simulations, and the periodic boundary conditions were used in three dimensions to mimic the crystalline periodicity. A spherical cutoff length of 19.0 Å was used in all simulations to evaluate the intermolecular LJ interactions without long-range corrections. The Coulombic interaction between CO₂ and adsorbent was accounted for using the Ewald sum technique.

For CO₂ molecules, the Coulombic interaction was calculated directly on the basis of the center-of-mass cutoff of 19.0 Å, because CO₂ molecule is neutral with the quadrupole interaction, which converges rapidly with the cutoff distance. To accelerate the simulation, the LJ and Coulombic interactions between adsorbate and adsorbent were calculated on the basis of a pretabulated energy map with a grid of 0.2 × 0.2 × 0.2 Å cubic mesh constructed throughout the unit cell of adsorbent.

The number of Monte Carlo trial moves used in a typical simulation was 6 million, though additional moves were used at high pressures. The first half of these moves was used only for equilibration and the second half was used for calculating the ensemble averages. For pure CH₄, three types of moves were randomly attempted—translation, insertion, and deletion. For pure CO₂, an additional move, rotation, was also included. For CO₂/CH₄ mixture, in addition to the above-mentioned moves, species exchange was also included with equal probability to ensure microscopic reversibility. In this latter move, one random selected sorbate molecule is exchanged with the other type of sorbate molecule. While this move is not a requirement in GCMC for mixtures, its use allows fast equilibration and reduces statistical errors after equilibration.

At specified T, V, and μ, GCMC simulation gives the absolute number of molecules adsorbed N_ads. However, experiment data are usually reported as the excess amount of adsorption N_ex. To make a comparison, the experimental N_ex was converted into N_ads by

\[ N_{\text{ads}} = N_{\text{ex}} + \rho_b V_{\text{free}} \]  

where ρ_b is the density of bulk gas calculated with PR EOS, and V_free is the free volume within adsorbent for adsorption estimated from

\[ V_{\text{free}} = \int_0^V \exp[-u_{\text{ad}}^{\text{He}}(r)/k_B T] \, dr \]  

where u_{\text{ad}}^{\text{He}} is the interaction between a single helium atom and adsorbent. In this calculation, \( u_{\text{ad}}^{\text{He}} = 2.58 \) Å and \( k_B T = 10.22 \) K were used. The free volume detected by helium is temperature-dependent, and usually the room temperature is chosen. The porosity of an adsorbent can be estimated by \( V_{\text{free}}/V_{\text{total}} \), with \( V_{\text{total}} \) the total occupied volume.

From the loading dependence of the total adsorption energy U_ad, the isosteric heat of adsorption q_{st} was calculated by the difference between the enthalpy of adsorbate in gas-phase \( H_b \) and the partial molar energy of the adsorbed phase.

\[ q_{\text{st}} = H_b - \left( \frac{\partial (U_{\text{ad}} - U_{\text{ani}})}{\partial N_{\text{ad}}} \right)_{T,V} \]  

where \( H_b \) can be approximated as RT, \( U_{\text{ad}} \) includes contributions from both adsorbate—adsorbent and adsorbate—adsorbate interactions, and \( U_{\text{ani}} \) is the intramolecular energy of the adsorbate molecules and is equal to zero for rigid molecules. The partial derivative in q_{st} can be calculated in GCMC simulations by fluctuation theory or direct differentiation of the simulation results. In this work, the latter was used.

### IV. Results and Discussion

**Adsorption of Pure CO₂ and CH₄**

Table 2 gives the density and porosity of MFI, C₁₆₈ schwarzite, and IRMOF-1 as well as the limiting heats of adsorption \( q_{\text{st}} \) and Henry constants \( K_b \) of pure CO₂ and CH₄ in each adsorbent. The density decreases in the order of MFI > C₁₆₈ > IRMOF-1, which is opposite to the porosity. For CO₂ and CH₄, both \( q_{\text{st}} \) and \( K_b \) are largest in C₁₆₈ and are smallest in IRMOF-1. The fact that the limiting properties in C₁₆₈ are larger than in the less porous MFI indicates that there is no direct relation between adsorption affinity and porosity. In a given adsorbent, both \( q_{\text{st}} \) and \( K_b \) of CO₂ are larger than those of CH₄, implying that CO₂ is more strongly adsorbed. This is not unexpected because CO₂ is a three-site molecule and has a greater interaction with adsorbent. Also for CH₄ in MFI, our simulated \( q_{\text{st}} \) is consistent with several reported values.

For CO₂ in MFI, \( q_{\text{st}} \) is in close agreement with previous experimental (24.07 kJ/mol) and simulation results, however, it is slightly lower than one reported value (27.2 kJ/mol). For CH₄ in IRMOF-1, again, our \( q_{\text{st}} \) agrees well with the reported simulated values.

Simulated and available experimentally measured adsorption isotherms of pure CO₂ and CH₄ separately in MFI, C₁₆₈ schwarzite, and IRMOF-1 are shown in Figure 3 as a function of the bulk pressure. All isotherms are of type I (Langmuirian), which is the characteristic of a microporous adsorbent with pores of molecular dimensions (below 2 nm). In MFI, the extent of CO₂ adsorption is consistently greater than that of CH₄. The simulated isotherms match closely with the experimental results for both CH₄ and CO₂, though deviations are observed at high pressures for CH₄ adsorption. In IRMOF-1, CO₂ adsorption is again consistently larger than CH₄ adsorption, as in MFI. At low pressures, the adsorption of both CO₂ and CH₄ is nearly negligible in IRMOF-1, since their interactions with the IRMOF-1 framework are weak, as evidenced from \( q_{\text{st}} \) and \( K_b \) in Table 2. The simulated isotherms are in accord with previous simulation results and experimental data, especially at low pressures. At high CO₂ pressures, simulation slightly overestimates the measured values.

### Table 2. Density and Porosity of MFI, C₁₆₈, and IRMOF-1. Limiting Adsorption Properties of Pure CH₄ and CO₂

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Density (g/cm³)</th>
<th>Porosity</th>
<th>Adsorbate</th>
<th>( q_{\text{st}} ) (kJ/mol)</th>
<th>( K_b ) (mmol/g/kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI</td>
<td>1.793</td>
<td>0.37</td>
<td>CH₄</td>
<td>19.42</td>
<td>0.010</td>
</tr>
<tr>
<td>C₁₆₈</td>
<td>1.294</td>
<td>0.67</td>
<td>CH₄</td>
<td>26.78</td>
<td>0.218</td>
</tr>
<tr>
<td>IRMOF-1</td>
<td>0.593</td>
<td>0.82</td>
<td>CH₄</td>
<td>10.31</td>
<td>0.0046</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
<td>35.67</td>
<td>1.215</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
<td>14.38</td>
<td>0.0093</td>
</tr>
</tbody>
</table>


A dual-site Langmuir–Freundlich (DSLF) equation was used to fit the adsorption isotherm of pure gas, where \( f \) is the fugacity of bulk gas at equilibrium with adsorbed phase, \( N_i \) is maximum loading in site \( i (=1 \text{ and } 2) \), \( k_i \) is the affinity constant, and \( n_i \) is used to characterize the deviation from the simple Langmuir equation. As shown below, the fitted parameters will then be used to predict the adsorption of mixture. There is no restriction on the choice of the model to fit the adsorption isotherm, but data over the pressure range under study should be fitted very precisely. The fitted isotherms are shown as solid lines in Figure 3, and the adjustable parameters are given in Table 3. For CO\(_2\) or CH\(_4\) in each adsorbent, the fit is nearly perfect.

![Figure 3](image)

**Figure 3.** Adsorption isotherms of CH\(_4\) and CO\(_2\) in MFI, C\(_{168}\), and IRMOF-1 as a function of bulk pressure. The filled symbols are simulation results, the lines are fits of the dual-site Langmuir–Freundlich equation to simulation results, and the open symbols are experimental data.

perfect, pure crystalline material, whereas experimental samples usually contain impurities and defects leading to a decrease in the storage capacity. In addition, the empirical force fields used may not be accurate enough to describe such a small discrepancy. In C\(_{168}\) schwarzite, CO\(_2\) is preferentially adsorbed at low pressures because CO\(_2\) has three interactions sites and is more energetically favored. At high pressures near saturation, the smaller molecule CH\(_4\) can fit into the partially occupied pores more easily; as a consequence of this entropic effect, CH\(_4\) is adsorbed more. However, CO\(_2\) is more greatly adsorbed than CH\(_4\) in MFI and IRMOF-1 over the entire pressure range under the study, in which the saturation has not been approached. This is because the partially charged CO\(_2\) has much stronger interactions with charged frameworks MFI and IRMOF-1, compared with the neutral adsorbent C\(_{168}\) schwarzite. Nevertheless, it is expected that at even higher pressures close to saturation, CH\(_4\) may have greater adsorption because of the entropic effect.

\[
N^o(f) = \frac{N_1 k_1 f^{n_1}}{1 + k_1 f^{n_1}} + \frac{N_2 k_2 f^{n_2}}{1 + k_2 f^{n_2}}
\]

(4)

was used to fit the adsorption isotherm of pure gas, where \( f \) is the fugacity of bulk gas at equilibrium with adsorbed phase, \( N_i \) is maximum loading in site \( i (=1 \text{ and } 2) \), \( k_i \) is the affinity constant, and \( n_i \) is used to characterize the deviation from the simple Langmuir equation. As shown below, the fitted parameters will then be used to predict the adsorption of mixture. There is no restriction on the choice of the model to fit the adsorption isotherm, but data over the pressure range under study should be fitted very precisely. The fitted isotherms are shown as solid lines in Figure 3, and the adjustable parameters are given in Table 3. For CO\(_2\) or CH\(_4\) in each adsorbent, the fit is nearly perfect.

A comparison of the CH\(_4\) adsorption isotherms in the three different adsorbents is presented in Figure 4 as a function of bulk pressure. It can be seen clearly that among the three adsorbents the greatest extent of adsorption is in IRMOF-1, which is not yet saturated even at the highest pressure considered here. This indicates that IRMOF-1 has a very high storage capacity for CH\(_4\). Also, the simulation results of CH\(_4\) in MFI and IRMOF-1 are in good agreement with experimental data. For CH\(_4\) in C\(_{168}\) schwarzite, no experimental data is available. Figure 5 shows the simulated and experimental adsorption isotherms for CO\(_2\) in MFI, C\(_{168}\) schwarzite, and IRMOF-1. As for CH\(_4\), there is greater adsorption of CO\(_2\) in IRMOF-1 than in MFI and C\(_{168}\) schwarzite. Recently, the U.S. Department of Energy (DoE) set the storage target for CH\(_4\) at 35 bar as 180 v/v,\(^{51}\) which is the excess volume of CH\(_4\) adsorbed at the standard temperature and pressure per volume of the storage vessel. We simulated excess adsorption of CH\(_4\) at 35 bar is 140.3 v/v, slightly greater than the experimental result of 121.9 v/v.\(^{47}\) Though the predicted CH\(_4\) storage in IRMOF-1 is lower than the DoE target, the capacity is significantly higher than in MFI and C\(_{168}\) schwarzite. On the basis of this observation, IRMOF-1 could be an ideal starting material for the storage of CH\(_4\) as well as for CO\(_2\). With a proper choice of an organic linker, it may be possible to design an MOF with enhanced storage capacity and reach the DoE target.

Figure 6a shows the isosteric heats of adsorption of CO\(_2\) and CH\(_4\) in MFI. Consistent with the adsorption isotherm, CO\(_2\) has higher heat of adsorption than CH\(_4\). With increasing loading, \( q_a \) initially increases, passes through a maximum at high loading, and finally decreases, though the extent of the change for CH\(_4\) is weaker. This type of behavior has been observed in experimental studies, for example, in the adsorption of Xe in zeolites X and Y,\(^{50}\) of Ar in AlPO\(_4\)-5,\(^{53}\) and of CH\(_4\) in an fcc-structured silica gel.\(^{39}\) The initial increase in \( q_a \) is attributed to the cooperative attractive interactions between adsorbate molecules, while the interaction between adsorbate and adsorbent remains nearly unchanged. The additional adsorbed adsorbate molecules must occupy the less favorable sites leading to a weaker adsorbate–adsorbent interaction, and the adsorbate–adsorbent interaction becomes less attractive because of the shorter separation distance. As a consequence, \( q_a \) tends to decrease at high loadings. Also included in Figure 6a are the experimentally determined \( q_a \) at

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low loadings. While our simulated limiting heats of adsorption $q_{st}$ as listed in Table 1 well reproduce the measured values, the heats of adsorption $q_{st}$ at low loadings seem to be underestimated. Figure 6b shows $q_{st}$ of CO$_2$ and CH$_4$ in C$_{168}$ schwarzite. The heat of adsorption in C$_{168}$ schwarzite shows different behavior in that with increasing coverage, $q_{st}$ first decreases to a minimum, then increases to a maximum, and finally decreases. Such behavior is not unusual and has been observed experimentally, such as in the adsorption of N$_2$ and CO in AlPO$_4$-5, of CH$_4$ in a silica gel with a hard-sphere structure, of Ar in chabazite, and of CH$_4$ in activated carbon. The initial decrease of $q_{st}$ is a consequence of the heterogeneous character of the C$_{168}$ schwarzite surface, in which the more energetically favorable sites for adsorption are occupied first, and then the less favorable sites are occupied as the loading increases. Figure 6c shows $q_{st}$ of CO$_2$ and CH$_4$ in IRMOF-1. The adsorption has not approached saturation, and as a result, $q_{st}$ increases monotonically with loading simply because of the increased cooperative interaction between adsorbate-adsorbate. However, a decrease in $q_{st}$ is expected at high loadings.

Figure 7 shows the equilibrium snapshots of the adsorbed CO$_2$ molecules at 500 and 2000 kPa in all the three adsorbents. In MFI, CO$_2$ are adsorbed mostly in the straight channels at a low pressure, however, at a high pressure CO$_2$ is also adsorbed in the zigzag channels. In C$_{168}$ schwarzite, CO$_2$ molecules occupy both the small and larger channels. As observed previously, on going from a low to a high pressure, the distribution of adsorbed...
CO$_2$ molecules changes from continuous in both channels to localized first in small channels and then in large channels. With increasing pressure, the adsorbate—adsorbate attraction first increases at low pressures, but then decreases. This is because as the number of admolecules increases, the channels become crowded and the separation distance between the admolecules decreases. In a competitive balance between energetic and entropic effects, a phenomenon similar to a first-order phase separation occurs, leading to the localized distribution in the channels, first in the small channels at modest pressures and then in the large pores at high pressures. In IRMOF-1, CO$_2$ molecules are concentrated around the metal—oxide tetrahedra. At a high pressure, CO$_2$ molecules also enter the straight channels within the framework.

**Adsorption of CO$_2$/CH$_4$ Mixture.** For adsorption of a gas mixture, the equilibrium condition is the equality of fugacity in the gas and adsorbed phases:

$$P_y f_i = x_i y_i f_i^o$$

where $P$ is bulk pressure, and $y$ and $x$ are the molar fraction in gas and adsorbed phases, respectively. The fugacity coefficient of component $i$ in gas phase is $\phi_i$ calculated by PR EOS, $f_i^o$ is the fugacity of pure component $i$ in a standard state, and $\gamma_i$ is the activity coefficient of component $i$ in the adsorbed phase. If a perfect mixing is assumed in the adsorbed phase and hence $\gamma_i = 1$, we can use the ideal-adsorbed solution theory (IAST) to predict the adsorption of a mixture on the basis of the information for pure components. The standard state is specified by the surface potential $\Phi_i$ given by the Gibbs adsorption approach

$$\Phi_i = -RT \int_0^{f_i^o} N_i^o(f) d\ln f_i$$

where $N_i^o(f)$ is the adsorption isotherm of pure component i. The mixing process is carried out at a constant surface potential $\Phi_1 = \Phi_2 = \cdots = \Phi$.

$S_{ij} = \left( \frac{x_i}{x_j} \right) \left( \frac{y_j}{y_i} \right)$

where $x_i$, $y_i$ are the mole fractions of component $i$ in the adsorbed and bulk phase, respectively. Although the general trend of selectivity can be properly estimated from simulation, it is remarked that the value of selectivity may not be as accurate as isotherm because a slight deviation in the number of adsorbed molecules may result in a larger deviation in selectivity.

Figure 9 shows the simulated adsorption selectivity of an equimolar mixture of CO$_2$ and CH$_4$ in MFI, C$_{168}$ schwarzite, and IRMOF-1 as a function of total bulk pressure. At a fixed total bulk pressure, selectivity is only a weak function of the bulk phase composition. In all the three adsorbents, the selectivity increases slowly at low pressures, then decreases at modest pressures, and finally increases slightly at high pressures. In C$_{168}$ schwarzite, the selectivity drops at high pressures.

Figure 8 shows the adsorption isotherms for an equimolar mixture of CH$_4$/CO$_2$ in MFI, C$_{168}$ schwarzite, and IRMOF-1 as a function of total bulk pressure. The closed symbols are from simulation and the lines are from IAST theory. In all adsorbents, CO$_2$ is more preferentially adsorbed than CH$_4$ as expected because of the stronger interaction between CO$_2$ and surfaces. Again, in IRMOF-1 the loading at low pressures is negligible. The agreement between IAST predictions and simulation results is generally good, particularly, at low pressures because IAST becomes exact in the Henry law limit. However, at high pressures IAST either underestimates or overestimates the results compared to simulation. This may be attributed to the assumption intrinsically used in IAST, that is, that the adsorbed phase of mixture is an ideal phase with perfect mixing. Improved predictions can be obtained by removing this assumption.

**Adsorption selectivity in a binary mixture of component i and j is defined as**

$S_{ij} = \left( \frac{x_i}{x_j} \right) \left( \frac{y_j}{y_i} \right)$

where $x_i$, $y_i$ are the mole fractions of component $i$ in the adsorbed and bulk phase, respectively. Although the general trend of selectivity can be properly estimated from simulation, it is remarked that the value of selectivity may not be as accurate as isotherm because a slight deviation in the number of adsorbed molecules may result in a larger deviation in selectivity.

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**Figure 7.** Snapshots of pure CO$_2$ adsorption in MFI, C$_{168}$, and IRMOF-1 at 500 kPa (top) and 2000 kPa (bottom).

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pressures since CO$_2$ nearly reaches saturation while there is still a slight increase in CH$_4$ adsorption. In IRMOF-1, the selectivity first remains nearly constant and then increases as pressure increases, which is consistent with the adsorption behavior seen above. The selectivity in C$_{168}$ schwarzite is the highest among the three adsorbents, though the adsorption capacity in IRMOF-1 is the highest.

V. Conclusions

We have used Monte Carlo simulation to study the adsorption of pure and mixed CO$_2$ and CH$_4$ in three nanosized porous adsorbents, silicalite, C$_{168}$ schwarzite, and IRMOF-1. The simulated adsorption isotherms and isosteric heats are consistent with available experimental data. Compared to silicalite and C$_{168}$ schwarzite, the adsorption capacity of pure CH$_4$ and CO$_2$ separately in IRMOF-1 is substantially higher. CO$_2$ is preferentially adsorbed over CH$_4$ from their binary mixture in all three adsorbents. Predictions from the ideal-adsorbed solution theory on the basis of the adsorption of only pure gases agree well with the simulation results.

Even though the storage capacity of IRMOF-1 is greater than silicalite and C$_{168}$ schwarzite, the adsorption selectivity of CO$_2$ over CH$_4$ is found to be close in all the three adsorbents. It would be of interest to find a porous material showing both high storage capacity and high selectivity. While in this work we only focus on IRMOF-1 as a prototype MOF, the study of different MOFs will also be performed as the functionality of MOFs can be tuned at the atomic scale by changing the metal–oxide and the organic linker. Moreover, here we investigate the selectivity on the basis of adsorption equilibrium; in the future, we will explore the selectivity on the basis of diffusion to determine the kinetic selectivity in different adsorbents.

Acknowledgment. The authors are grateful for the support from the National University of Singapore, the U.S. National Science Foundation, and the U.S. Department of Energy.

LA062289P