Molecular Simulation Studies of CO$_2$ Adsorption by Carbon Model Compounds for Carbon Capture and Sequestration Applications

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Supporting Information

ABSTRACT: Effects of oxygen-containing surface functionalities on the adsorption of mixtures including CO$_2$/CH$_4$, CO$_2$/N$_2$, and CO$_2$/H$_2$O have been investigated in the current work. Together with Bader charge analysis, electronic structure calculations have provided the initial framework comprising both the geometry and corresponding charge information required to carry out statistical-based molecular simulations. The adsorption isotherms and selectivity of CO$_2$ from CO$_2$/N$_2$, CO$_2$/CH$_4$, and CO$_2$/H$_2$O gas mixtures were determined by grand canonical Monte Carlo simulations at temperature/pressure conditions relevant to carbon capture and sequestration applications. The interactions between the surfaces with induced polarity and nonpolar/polar molecules have been investigated. It has been observed that, due to the induced polarity of the surface functionalization, the selectivity of CO$_2$ over CH$_4$ increases from approximately 2 to higher than 5, and the selectivity of CO$_2$ over N$_2$ increases from approximately 5 to 20, especially in the low-pressure regime. However, water vapor will always preferentially adsorb over CO$_2$ in carbon-based systems containing oxygen functionalized surfaces at conditions relevant to carbon capture application. Molecular simulation results indicate that the surface chemistry in micropores is tunable thereby influencing the selectivity for enhanced uptake of CO$_2$.

1. INTRODUCTION

To stabilize the atmospheric CO$_2$ emissions at a level that could minimize the impact on the global climate, CO$_2$ capture and sequestration (CCS) provides a bridging strategy to the development of carbon-free energy systems. In the case of carbon capture, our previous studies have shown that carbon-based sorbents may be competitive with other sorbents in terms of the pure CO$_2$ adsorption capacity by modifying the surface functionality.\(^1\) In the case of carbon storage in coal and the organic matrix of gas shale, CO$_2$ injection into coalbeds and gas-shale reservoirs may enhance subsequent natural gas (e.g., primarily methane (CH$_4$)) recovery while simultaneously storing CO$_2$. At the molecular-scale, both carbon capture and storage processes share a major challenge, that is, an insufficient fundamental understanding of the processes involving CO$_2$ adsorption in the micropores of carbon-based systems and the subsequent difficulties in predicting the adsorption selectivity of CO$_2$ in a complex gas mixture under different temperature and pressure conditions. In the current study, two systems including CO$_2$ have been investigated. Mixtures of CO$_2$/CH$_4$ and CO$_2$/N$_2$ are important practical systems that are included in large-scale industrial applications: the CO$_2$/CH$_4$ system is involved in CO$_2$ enhanced coalbed methane recovery (CO$_2$-ECBM) and CO$_2$ enhanced shale gas production, while the CO$_2$/N$_2$ system is applicable to CO$_2$ separation from flue gas mixtures of coal- or natural gas-fired power plants.\(^2,3,4\)

The adsorption of a single-component system is relatively straightforward and has been fully investigated in the literature. However, less information related to multicomponent adsorption processes is available, which is more practical to the real CCS applications. The interactions between different gas-phase species and the polarity of the gas species may affect the adsorption process, which is also essential in predicting carbon capture from mixtures in addition to CO$_2$ storage potential.

Jorge et al.\(^5\) simulated adsorption isotherms for mixtures of nonpolar (ethane) and polar (water) species in slit-shaped activated carbon pores in the temperature range of 273–323 K. The presence of carbonyl sites on the pore walls was taken into consideration to introduce a degree of chemical heterogeneity. The results indicated that the presence of carbonyl sites enhances water adsorption in the pore. Shevade et al.\(^6,7\) studied the adsorption behavior of a water–methanol mixture in slit carbon (graphite) and in uncharged alumino-silicate micropores at 298 K. The results of their work showed that graphite and uncharged silicate surfaces are covered by a dense layer of adsorbed water and methanol molecules having a weakened hydrogen-bonding network. In the interior of the pore, the fluid exhibits bulk-like behavior with a stronger hydrogen bonded structure with preferential adsorption of water over methanol.

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The density of adsorbed water and methanol near the graphite surface is greater than that near the uncharged silicate surface. To investigate the effects of different pore structure models and interaction parameters on the adsorption of the CO2/CH4 mixture, Nicholson et al. compared two pore structure models, that is, slit-shaped pore and cylindrical-shaped pores using the grand canonical Monte Carlo method. The selectivity of CO2 over CH4 was calculated as a function of pore size using different pore and interaction models. The selectivity was found to be a maximum between pore widths of 6–8 Å for slit pore and at a pore radius around 5 Å for cylindrical pores. The slit and cylindrical pore models studied show several differences that can be attributed mainly to geometrical effects arising from the greater constraint on the freedom of rotation for the CO2 molecule in the cylindrical geometry. However, it was demonstrated that energetic effects play a major role in determining selectivity. Kurniawan et al. focused on high-pressure single and binary gas adsorption of CO2 and CH4 in an idealized slit pore system, with the simulation conditions reasonable for deep CBM reservoirs, that is, temperatures of 308 K, 318 K, and 348 K, pressures up to 100 bar, and pore widths in the range of 7–75 Å. The adsorption of CO2 is preferred over CH4 from binary mixtures in the oxygen-containing functionalized slit pores were investigated by simulating gas adsorption in idealized functionalized carbon frameworks. The slit-pore surfaces were represented by the DFT-optimized perfect and functionalized graphitic slit pores.

Two types of surface functionalities were investigated in the current work. One is the monovacancy site hydrated by dissociated H2O due to the existence of water vapor in the gas-phase environment and the potential existence of undercoordinated carbon atoms in the carbon pore structures, and another is with respect to the inherent oxygen-containing functional groups which were developed as the natural systems formed over time. The investigated systems include a perfect graphite basal plane surface, a hydrated graphite surface, and five oxygen-containing functionalized-graphite surfaces, each with unique vacancy sites or functional groups as shown in Figure 1. The details of these functional groups can be found in our previous work.

Electronic structure calculations of functionalized carbon surfaces were carried out to optimize the functionalized graphitic surfaces using the Vienna ab initio simulation package (VASP). The investigated functional groups were positioned on either a 6 × 6 (e.g., hydrated graphite surface) or a 4 × 4 (e.g., other embedded oxygen-contained functionalized surfaces) carbon-ring unit cell with functional groups located in the center of the top graphene layer. Plane-wave electronic density functional theory was employed due to its balanced computational efficiency and reasonable accuracy in predicting the partial charge distributions. The DFT calculations coupled with a van der Waals-inclusive correction (DFT-D) were
carried out to calculate the energies associated with the interlayer interactions of graphitic structures, and the corresponding partial charge values associated with the top layer atoms were compared with the values given by DFT calculations without the corrections. The projector augmented wave (PAW) potential, was used to describe the core–valence electron interaction of the carbon and oxygen atoms. The model of Perdew, Burke, and Ernzerhof (PBE) was employed for the nonlocal corrections and a Monkhorst-Pack k-point sampling grid with a plane-wave cutoff of 750 eV was used. An idealized perfect and functionalized carbon-based pore surface was represented by a 3-layer graphite slab. Given the periodic boundary conditions, a vacuum region of 20 Å between the slabs was used to prevent interactions between the periodic images.

Bader charge analysis was undertaken to calculate the partial charge distributions of the perfect graphite and the functionalized graphite surfaces, which were required for the energy contributions in the statistical model simulations. The optimized geometries and the partial charge distributions were assigned to the surface atoms of the slit pore in the molecular simulations to investigate various gas mixture adsorption configurations. The optimized 3-layer graphitic slab was employed in the molecular simulations to represent the wall of the slit pores. The DFT-optimized unit cells were repeated to construct the pore walls of the slit pore in the GCMC simulations. The simulation box containing the slit pore has dimensions of $30 \times 26 \times 33$ Å, and the periodic boundary conditions were applied in the x- and y-directions. A distance of 20 Å between the two slabs in the z-direction was used to model the width of the slit pore and to avoid interactions between the functional groups on the opposing pore walls. To allow for a fair comparison among various functionalities, the O:C ratio of all functionalized surfaces was kept as 1:24, with the exception of the basal plane and hydrated graphite surfaces.

For both lab measurements and molecular simulations, it is essential to accurately determine the pore volume available for adsorption. Given that helium is a nonadsorbing gas (or very weakly adsorbing gas), the pore volume is typically determined using helium at ambient temperature before initiating adsorption experiments. While the pore volume accessed by helium is not necessarily the same as that by CO$_2$ at the same temperature and pressure conditions, the helium pore volume measurements may accurately describe the trend associated with the pore volume as it is influenced by the various functional groups. The helium pore volume measurements were conducted using GCMC in this work for consistency with experimental work, in which helium pore volume measurements are widely used. The detailed algorithm associated with the pore volume calculation using helium is available in the Supporting Information.

2.2. Force Field. Physisorption processes of CO$_2$ in microporous carbons are predominantly associated with van der Waals forces (also known as dispersion-repulsion forces) and electrostatic forces (also known as Columbic interactions), which are sourced mainly from permanent dipole, quadrupole, and higher-induced-pole interactions. The van der Waals forces are present in all systems, but the electrostatic interactions are only present in systems that contain charges, such as charges due to surface functional groups or surface defects.

To describe the adsorption of pure components and mixtures of CO$_2$, CH$_4$, and N$_2$ molecules in the functionalized graphitic slit pores, CH$_4$ was simply treated as a one-center Lennard-Jones molecule because the CH$_4$ molecule has relatively weak octupole moment. The CO$_2$ molecule was modeled using the TraPPE model, which is a three-site rigid model that accounts for the intrinsic quadrupole moment of CO$_2$ using a partial charge at each site. The partial charges on C and O atoms are $q_C = 0.70 \epsilon$ and $q_O = -0.35 \epsilon$ ($\epsilon = 1.6022 \times 10^{-19}$ C), respectively. The CO$_2$ molecule has a C=O bond length of 1.16 Å, with an O=C=O bond angle of 180.0 degrees. The N$_2$ molecule was represented as a three-site model with two sites located at two N atoms with the third located at its center of mass (COM), with a bond length between the two N atoms of 1.098 Å. Each N$_2$ molecule was assigned a negative charge on each N atom, that is, $q_N = -0.482 \epsilon$ and a positive charge at the COM site, that is, $q_{\text{COM}} = 0.964 \epsilon$. The H$_2$O molecule was simulated using the TIP3P model, which is a three-site rigid model that accounts for its intrinsic dipole moment. The partial charges on H and O atoms are $q_H = 0.417 \epsilon$ and $q_O = -0.834 \epsilon$, respectively; the H—O bond length is 0.957 Å, with an H—O—H bond angle of 104.52 degrees.

The potential energies associated with different LJ sites were calculated using standard Lorentz–Berthelot mixing rules. As shown in Table 1, the LJ parameters for the other species contained within the surface functional groups were taken from previous molecular simulation studies of Tenney and Lastoskie, where $\epsilon_{ij}/k_B$ is the depth of the potential well, $\sigma_{ij}$ is the finite distance at which the interparticle potential is zero. The CO$_2$–CO$_2$ interactions and the interactions between CO$_2$/CH$_4$/N$_2$ and the functionalized graphitic surface atoms were modeled as a combination of Lennard-Jones (LJ) and Columbic potentials, where the van der Waals interactions between two Lennard-Jones (LJ) sites were calculated using the Bader charge analysis. It would be more accurate to carry out ab initio simulations in the future work to optimize the LJ potential parameters $\epsilon$ and $\sigma$ at the various LJ sites of the functional groups, including a more accurate $\sigma$ value for the hydrogen atoms, which is essential for accurately predicting the possible hydrogen-bonding interactions between the surface functional groups and the adsorbates, such as H$_2$O molecules.

2.3. Molecular Simulations. Grand canonical Monte Carlo (GCMC) simulations of CO$_2$ adsorption in idealized organic microporous carbons were carried out in the $\mu$VT ensemble. In the current work, to focus on the effect of the surface functionalities and the selectivity of CO$_2$ from CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas mixtures, a temperature of 298 K and a pressure of up to 300 bar were investigated, conditions relevant to CCS applications. The mixture fugacities required as simulation inputs were calculated using the Peng–Robinson Table 1. Potential Parameters for Force Field Calculations

<table>
<thead>
<tr>
<th>Force Field</th>
<th>$\epsilon_{ij}/k_B$ [K]</th>
<th>$\sigma_{ij}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TraPPE $^{19}$</td>
<td>C(CO$_2$)</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>O(CO$_2$)</td>
<td>79</td>
</tr>
<tr>
<td>1CLJ $^{19}$</td>
<td>CH$_4$</td>
<td>148</td>
</tr>
<tr>
<td>TraPPE $^{21}$</td>
<td>N($N_2$)</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>COM($N_2$)</td>
<td>7.65</td>
</tr>
<tr>
<td>TIP3P $^{22}$</td>
<td>H(H$_2$O)</td>
<td>76.58</td>
</tr>
<tr>
<td></td>
<td>O(H$_2$O)</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>C(graphite)</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>O(surface functional groups) $^{24}$</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>H(surface functional groups) $^{24}$</td>
<td>30</td>
</tr>
</tbody>
</table>
equation of state. To speed up the convergence, energy-biased insertions of the sorbate molecules were employed and acceptance ratios for insertions and deletions were above 1% (slightly lower at the higher loadings) to ensure reasonable equilibration in the GCMC simulations. A total of 100 million GCMC moves were attempted during each GCMC simulation. To reduce the computational time, a rigid graphite framework was assumed. The rigid framework assumption is based on the fact that the graphitic structures have been optimized in the plane-wave DFT calculations and that the geometries of the framework were not significantly influenced by CO₂ adsorption. Limitations of this simplistic approach will be considered in future work.

3. RESULTS AND DISCUSSION

3.1. Partial Charge Distribution and the Optimized Geometries of Perfect and Functionalized Graphitic Surfaces. In the current work, the partial charge distributions of two types of graphitic surfaces were investigated, one with the functional groups formed due to the competition of volatile components, that is, the competition of CO₂ with H₂O while interacting with the defect sites; and another with oxygen-containing functional groups embedded. As introduced in the previous work, the embedded oxygen atoms on each surface exhibit high electronegativities due to electron gain from the surrounding surface carbon atoms. For example, as shown in Figure 2, oxygen atoms contained within a carboxyl functional group have partial charges of $-1.106$ e and $-1.124$ e, and therefore have the highest potential among all the surface atoms to donate electrons to the neighboring adsorbate molecules. Within these scenarios, oxygen-containing functional groups seem to allow for enhanced electron donation and versatility depending on the acid–base nature of the adsorbate, with oxygen atoms acting as a Lewis base donating their electron density to the acidic carbon atoms of CO₂ molecules. It is thus expected that the density of CO₂ molecules in the condensed phase will be enhanced in the functionalized slit pores due to the stronger Lewis basicity of the surface functional groups compared to the basicity associated with the π-electrons of the perfect graphite surface. Due to the higher electronegativities of the O atoms compared to the C atom of CO₂ molecules, the C atom will be more attracted to the embedded oxygen functional groups, and therefore, it is more likely that CO₂ molecules will rotate parallel to the oxygen-containing functional groups. The orientation of N₂ molecules will be similar to that of linear CO₂ molecules.

Also, it is expected that the packing pattern of adsorbed CO₂ and N₂ molecules will be influenced by the interaction with functional groups and that the adsorption mechanism will differ based upon the presence of embedded oxygen functional groups. The overall results of the Bader charge analyses for all of the functionalized surfaces investigated have been described in previous work. Based on the Bader charge analyses, graphitic slit pores with embedded carboxyl functional groups are hypothesized to more strongly influence surface–CO₂ interactions compared to the other functional groups investigated. The partial charge distributions of the other oxygen-containing surfaces and the hydrated surfaces can be found in the Supporting Information of the previous work.

3.2. Adsorption of CO₂/CH₄ and CO₂/N₂ Mixtures in Perfect and Functionalized Slit Pores. For pores 20-Å wide, the actual pore volume varies due to the different geometries of the functional groups present, even though the pore widths themselves are equal. To compare the density of the different adsorbed gas species of mixtures in various graphitic slit pores, the unit cell volumes of the micropores with the same pore width have been normalized. A complete comparison of pore volumes with different surface functionalities for 20-Å wide pores is available in the Supporting Information. It was observed that the pore volumes decrease up to approximately 15% due to the existence of the embedded functional groups.

In micropores such that the diameter is less than 20 Å, adsorption is governed by combined gas-surface and gas-gas interactions. The density of both gas species in the CO₂/CH₄ and CO₂/N₂ mixtures were compared to investigate the effect

<table>
<thead>
<tr>
<th></th>
<th>PG</th>
<th>OX</th>
<th>OH</th>
<th>C=O</th>
<th>C=O_COH</th>
<th>COH_C=O</th>
<th>COOH</th>
<th>MonoV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CH₄ (300 bar)</td>
<td>CO₂</td>
<td>density [mmol/cm³]</td>
<td>11.67</td>
<td>16.86</td>
<td>18.13</td>
<td>18.10</td>
<td>18.11</td>
<td>17.55</td>
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<tr>
<td></td>
<td>increase percentage [%]</td>
<td>44</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>50</td>
<td>56</td>
<td>−9</td>
</tr>
<tr>
<td>CH₄</td>
<td>density [mmol/cm³]</td>
<td>7.06</td>
<td>4.26</td>
<td>4.34</td>
<td>4.13</td>
<td>3.87</td>
<td>4.53</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>increase percentage [%]</td>
<td>−40</td>
<td>−39</td>
<td>−42</td>
<td>−45</td>
<td>−36</td>
<td>−36</td>
<td>−50</td>
</tr>
<tr>
<td>CO₂/N₂ (150 bar)</td>
<td>CO₂</td>
<td>density [mmol/cm³]</td>
<td>15.09</td>
<td>18.76</td>
<td>20.32</td>
<td>20.10</td>
<td>20.00</td>
<td>20.37</td>
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<td>33</td>
<td>33</td>
<td>35</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>N₂</td>
<td>density [mmol/cm³]</td>
<td>2.47</td>
<td>1.64</td>
<td>1.60</td>
<td>1.50</td>
<td>1.44</td>
<td>1.52</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>increase percentage [%]</td>
<td>−34</td>
<td>−35</td>
<td>−39</td>
<td>−42</td>
<td>−38</td>
<td>−49</td>
<td>−49</td>
</tr>
</tbody>
</table>

Figure 2. Partial charge distribution of carboxyl embedded graphitic surface. Gray, carbon atoms (cross represents bottom two layers); red, oxygen atom.

Table 2. Effect of Surface Functionality on the Adsorption of Gas Species in the Equimolar Mixtures at T = 298 K
of surface functionalities on selective gas adsorption. As shown in Table 2, in the case of the CO$_2$/CH$_4$ mixture, the oxygen-containing functional groups lead to an increase in the density of adsorbed CO$_2$, especially in the case of carboxyl functionalized graphitic slit pores, in which the density is increased by approximately 56%. Meanwhile, the adsorbed CH$_4$ density decreases by approximately 9% compared to that of the perfect graphite slit pore. On the other hand, the hydrated graphite was found to hinder CO$_2$ adsorption with enhanced CH$_4$ adsorption. In general, the physical adsorption forces include both dispersive and electrostatic (or Coulombic) types of forces in the charged system. In the nonpolar system, there are only dispersion forces; whereas in the polar system, the electrostatic forces can play an important role in adsorption. Due to the strong permanent quadrupole moment of CO$_2$ it will be preferentially attracted by negatively charged surface atoms, which causes an enhancement of CO$_2$ adsorption over CH$_4$ due to the nonpolarity of CH$_4$. This behavior is similar in the case of CH$_4$ and CO$_2$/N$_2$ gas mixtures at 298 K of the various functionalized slit pores, in which the density is increased by approximately 56%. Meanwhile, the adsorbed CH$_4$ density decreases by approximately 9% compared to that of the perfect graphite slit pore. On the other hand, the hydrated graphite was found to hinder CO$_2$ adsorption with enhanced CH$_4$ adsorption. In general, the physical adsorption forces include both dispersive and electrostatic (or Coulombic) types of forces in the charged system. In the nonpolar system, there are only dispersion forces; whereas in the polar system, the electrostatic forces can play an important role in adsorption. Due to the strong permanent quadrupole moment of CO$_2$ it will be preferentially attracted by negatively charged surface atoms, which causes an enhancement of CO$_2$ adsorption over CH$_4$ due to the nonpolarity of CH$_4$. This behavior is similar in the case of CH$_4$ and CO$_2$/N$_2$ gas mixtures at 298 K of the various functionalized slit pores, in which the density is increased by approximately 56%. Meanwhile, the adsorbed CH$_4$ density decreases by approximately 9% compared to that of the perfect graphite slit pore. On the other hand, the hydrated graphite was found to hinder CO$_2$ adsorption with enhanced CH$_4$ adsorption. In general, the physical adsorption forces include both dispersive and electrostatic (or Coulombic) types of forces in the charged system. In the nonpolar system, there are only dispersion forces; whereas in the polar system, the electrostatic forces can play an important role in adsorption. Due to the strong permanent quadrupole moment of CO$_2$ it will be preferentially attracted by negatively charged surface atoms, which causes an enhancement of CO$_2$ adsorption over CH$_4$ due to the nonpolarity of CH$_4$. This behavior is similar in the case of CO$_2$/N$_2$ mixtures at $p = 150$ bar, where N$_2$ has weaker polarity compared to that of CO$_2$.

To further explore the effect of surface functionality on the adsorption of gas mixtures, the selectivity of CO$_2$ from CO$_2$/CH$_4$ and CO$_2$/N$_2$ gas mixtures at 298 K of the various functionalized slit pores with a width of 20 Å is shown in Figures 3 and 4, respectively. Pressures of up to 300 and 150 bar, which are relevant to the storage conditions have been investigated. Selectivity of CO$_2$ from the gas mixture is defined as follows:

$$S_{\text{CO}_2/\text{CH}_4} = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{x_{\text{CO}_2}/x_{\text{N}_2}}, S_{\text{CO}_2/\text{N}_2} = \frac{x_{\text{CO}_2}/x_{\text{N}_2}}{x_{\text{CO}_2}/x_{\text{CH}_4}}$$

such that $S$ represents the selectivity of CO$_2$ of a gas mixture, $x_{\text{CO}_2}$ is the molar fraction of CO$_2$ in the adsorbed phase, and $x_{\text{CH}_4}$ or $x_{\text{N}_2}$ represents the mole fraction of CH$_4$ or N$_2$ in the bulk gas phase. In the current study, the mole fraction of CO$_2$ and other gas species (e.g., CH$_4$ or N$_2$) are both kept as 0.5, with an estimated selectivity greater than 1 indicating that CO$_2$ preferentially adsorbs over the other gas species throughout the adsorption process. It has been observed that, due to the induced polarity of the surface functionalization, the selectivity of CO$_2$ over CH$_4$ increases from approximately 2 to higher than 5, especially in the low-pressure region. The selectivity of CO$_2$ over CH$_4$ in a perfect graphite slit pore is consistent with the values reported by Heuchel et al. and Nicholson, which are in the range of 1−4 under similar conditions. Due to the induced polarity of a functionalized surface, CO$_2$ will always preferentially adsorb over CH$_4$ due to the quadrupole moment of CO$_2$ (i.e., $-13.7 \times 10^{-40}$ Coulomb·m$^2$). Tetrahedral molecule CH$_4$ has a zero dipole and quadrupole moment but with a permanent octupole moment, which has a weaker effect than the quadrupole moment. This behavior is consistent with the Bader charge analysis results.

Similarly, the selectivity of CO$_2$ over N$_2$ increases from approximately 5 to 20. The higher selectivity of CO$_2$ over N$_2$ compared to that of CO$_2$ over CH$_4$ is consistent with the research carried out by Heuchel et al. and the experimental adsorption measurements of gas mixtures in coal by Hall et al. The quadrupole moment of N$_2$ is $-4.9 \times 10^{-40}$ Coulomb·m$^2$, which is lower than that of CO$_2$. Therefore, CO$_2$ preferentially adsorbs over N$_2$ to the functionalized surfaces due to the stronger polarity.

In addition to the investigation of mixtures including N$_2$ and CH$_4$, the existence of water vapor was also considered. As water vapor is present in flue gas at an approximate 10% concentration compared with CO$_2$ at $\sim$12−14%, and water also coexists with methane in coal-bed methane and shale gas reservoirs, the existence of water is crucial for providing an accurate description of CO$_2$ adsorption for CCS applications. As shown in Table 3, due to the induced polarity of the surface functionalization, water vapor will always preferentially adsorb over CO$_2$ to these surfaces. As an example, the selectivities of CO$_2$ over water vapor were compared at 333 K and 1 bar, which is relevant to flue gas conditions. The selectivity is above 1 when the gas mixture is adsorbed on perfect graphite.

![Figure 3](image1.jpg) Selectivity of CO$_2$ over CH$_4$ from the CO$_2$/CH$_4$ mixture in slit pores with different embedded surface functional groups.

![Figure 4](image2.jpg) Selectivity of CO$_2$ over N$_2$ from the CO$_2$/N$_2$ mixture in slit pores with different embedded surface functional groups.

Table 3. Effect of Surface Functionality on the Selectivity of CO$_2$ from CO$_2$/H$_2$O Mixture

<table>
<thead>
<tr>
<th>functional group</th>
<th>density of adsorbed CO$_2$ (mmol/cm$^3$)</th>
<th>density of adsorbed H$_2$O (mmol/cm$^3$)</th>
<th>selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>perfect graphite</td>
<td>0.19</td>
<td>0.026</td>
<td>7.2124</td>
</tr>
<tr>
<td>epoxy functionalized</td>
<td>0.01</td>
<td>0.25</td>
<td>0.0002</td>
</tr>
<tr>
<td>hydroxyl functionalized</td>
<td>0.002</td>
<td>55.56</td>
<td>0.0000</td>
</tr>
<tr>
<td>hydrated graphite</td>
<td>2.86</td>
<td>0.34</td>
<td>8.5352</td>
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</table>

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and hydrated graphite surfaces, whereas the values are far below 1 when the gas mixture is adsorbed in pores containing the oxygen-containing functional groups, which means H2O molecules uptake almost all the possible adsorption sites in the slit pores with charged surfaces, thereby allowing CO2 to diffuse through the functionalized slit pores without being adsorbed. The low selectivity of CO2 over H2O is due to the dipole moment of water having a stronger effect than the quadrupole moment of CO2.

Therefore, it is important to design sorbents that lead to the participation of water in binding as it will always be more “reactive” than CO2 based upon the inherent charge character of each of these molecules. A general noticeable shortcoming of adsorption-based CO2 separation processes is that competing gases like H2O may need to be removed upstream for adsorption processes due to its high polarity and subsequent preferential adsorption thereby reducing the sorbent’s capacity for CO2.

For an improved understanding of the distribution of different gas species adsorbed in the functionalized slit pores, the local density distribution of CO2 with CH4 and N2 in the functionalized graphitic pores are shown in Figure 5. It can be observed that the density of CO2 across the entire pore space increases, especially near pore walls. On the other hand, the density of CH4 and N2 in the condensed phase near the pore walls decreases due to the induced polarity of the surface functionalization, and therefore, adsorption is inhibited due to the strong attraction between CO2 and the charged surfaces.

Molecular simulations of the adsorption of CO2/CH4 and CO2/N2 mixtures show that CO2 is preferentially adsorbed on oxygen-containing functionalized graphitic surfaces with an induced polarity due to the strong quadrupole moment of CO2 compared with that of N2 and the weak octupole moment of CH4. For the mixtures where CO2 has a stronger polarity, the difference in the quadrupole moment of the mixture component results in a different surface occupancy on the same surface, and the oxygen-containing functionalized surfaces not only increase the total adsorption of CO2, but also enhance the separation selectivity of a given gas mixture.

4. IMPLICATIONS

Based on the GCMC simulations, the selectivities of CO2 over CH4 from a mixture of CO2/CH4 at pressures less than 5 bar and a temperature of 298 K are generally higher than 15, compared to current state-of-the-art sorbents, i.e., MOFs that range between 4 and 7 under the same conditions.33 The selectivity of CO2 from CO2/N2 gas mixtures has been calculated to be generally higher than 20 in the current work, and is approximately 20 at 20 bar and 298 K, compared to MOFs that range between 5 and 40 at the same temperature and pressure conditions.34 From these investigations it becomes evident that the surface chemistry is tunable thereby influencing the selectivity and allowing for controlled adsorption in carbon-based sorbents, implying that these materials may be competitive with other sorbents (e.g., zeolites, MOFs, etc.) in terms of the CO2 selectivity of gas mixtures including N2 and CH4. Although coal and synthetic porous carbon materials have different structures and surface chemistries, the molecular simulations assist in inferring the appropriate surface functionality for the synthesis of new materials with enhanced CO2 adsorption properties in addition to providing a deeper understanding of the adsorption mechanisms of existing natural and synthetic carbon systems.

■ ASSOCIATED CONTENT

* Supporting Information
Details of the prediction of pore volume by helium adsorption from calculation of the second virial coefficient and the comparison of the realistic pore volumes with different surface functionalities are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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