

Molecular Simulation Studies of CO₂ Adsorption by Carbon Model Compounds for Carbon Capture and Sequestration Applications

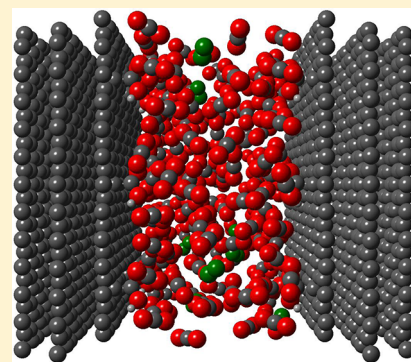
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S Supporting Information

ABSTRACT: Effects of oxygen-containing surface functionalities on the adsorption of mixtures including CO₂/CH₄, CO₂/N₂, and CO₂/H₂O 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 CO₂ from CO₂/N₂, CO₂/CH₄, and CO₂/H₂O 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 CO₂ over CH₄ increases from approximately 2 to higher than 5, and the selectivity of CO₂ over N₂ increases from approximately 5 to 20, especially in the low-pressure regime.

However, water vapor will always preferentially adsorb over CO₂ 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 CO₂.



1. INTRODUCTION

To stabilize the atmospheric CO₂ emissions at a level that could minimize the impact on the global climate, CO₂ 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 CO₂ adsorption capacity by modifying the surface functionality.¹ In the case of carbon storage in coal and the organic matrix of gas shale, CO₂ injection into coalbeds and gas-shale reservoirs may enhance subsequent natural gas (e.g., primarily methane (CH₄)) recovery while simultaneously storing CO₂. At the molecular-scale, both carbon capture and storage processes share a major challenge, that is, an insufficient fundamental understanding of the processes involving CO₂ adsorption in the micropores of carbon-based systems and the subsequent difficulties in predicting the adsorption selectivity of CO₂ in a complex gas mixture under different temperature and pressure conditions. In the current study, two systems including CO₂ have been investigated. Mixtures of CO₂/CH₄ and CO₂/N₂ are important practical systems that are included in large-scale industrial applications: the CO₂/CH₄ system is involved in CO₂ enhanced coalbed methane recovery (CO₂-ECBM) and CO₂ enhanced shale gas production, while the CO₂/N₂ system is applicable to CO₂ 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 CO₂ 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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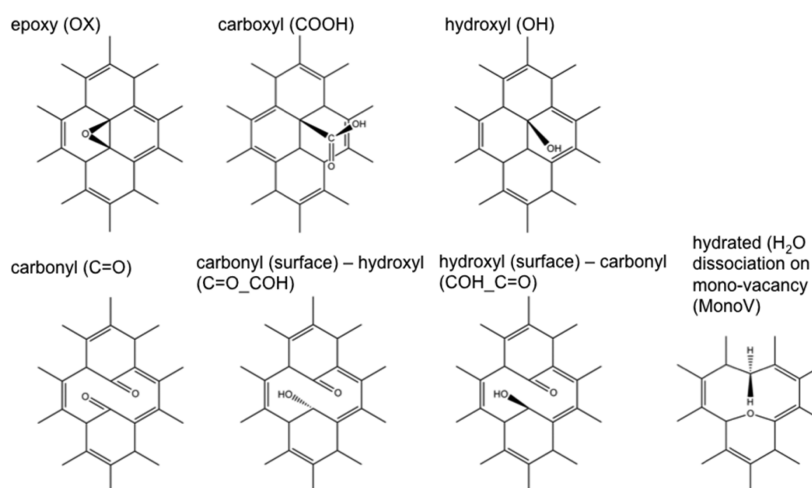


Figure 1. Functionalized graphitic surfaces investigated in the current work. These functional groups are positioned in the center of the top layer of the periodic graphite slabs.

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.⁸ 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.⁹ 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 under the investigated conditions. The selectivity of CO₂ with respect to CH₄ initially increases to a maximum value at an equivalent pressure and then decreases becoming constant when pressure is increased. This trend is weakly dependent on temperature, and higher selectivity is observed in the small pores because of the stronger interaction potential existing between the adsorbate and pore wall. Results from this previous work provide suggestions of optimal conditions for CO₂ storage for CBM reservoir applications. Compared to the research previously carried out on single-component adsorption, relatively few studies are implemented on multiple-component mixtures, in particular, including the effect of surface chemical heterogeneity on mixture adsorption for the application of CCS.

The objectives of this work were to evaluate the influence of realistic surface functional groups of carbon pore surfaces on the adsorption of gas mixtures including CO₂, CH₄, N₂, and H₂O. Plane-wave electronic structure calculations were performed to determine the electrostatic distribution and the optimized geometries of the functionalized carbon surfaces. A Bader charge analysis¹⁰ was undertaken to calculate the partial

charge distributions, which were required for the energy contributions in the statistical model simulations. In particular, Monte Carlo (MC) simulations were carried out within the Grand Canonical ensemble to predict the thermodynamic equilibrium properties of the gas-carbon pore system.

2. COMPUTATIONAL METHODOLOGY

2.1. Functionalized Graphitic Slit Pores.

In this work, complex pore structures for general carbon-based porous materials and natural organic materials have been modeled as a collection of independent, noninterconnected, functionalized graphitic slit pores with surface heterogeneities. The adsorption and the selectivity of CO₂ from CO₂/N₂ and CO₂/CH₄ gas mixtures in the oxygen-containing functionalized graphitic 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 under-coordinated 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.¹¹ 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.¹

Electronic structure calculations of functionalized carbon surfaces were carried out to optimize the functionalized graphitic surfaces using the Vienna ab initio simulation package (VASP),^{12,13} 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)¹⁴ 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,^{15,16} was used to describe the core–valence electron interaction of the carbon and oxygen atoms. The model of Perdew, Burke, and Ernzerhof (PBE)¹⁵ was employed for the nonlocal corrections and an $11 \times 11 \times 1$ Monkhorst-Pack¹⁷ 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 analysis¹⁰ 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 CO₂ 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 CO₂ 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.^{2,18}

To describe the adsorption of pure components and mixtures of CO₂, CH₄, and N₂ molecules in the functionalized graphitic slit pores, CH₄ was simply treated as a one-center Lennard-

Jones molecule because the CH₄ molecule has relatively weak octupole moment.¹⁹ The CO₂ molecule was modeled using the TraPPE model,²⁰ which is a three-site rigid model that accounts for the intrinsic quadrupole moment of CO₂ using a partial charge at each site. The partial charges on C and O atoms are $q_C = 0.70 e$ and $q_O = -0.35 e$ ($e = 1.6022 \times 10^{-19} C$), respectively. The CO₂ molecule has a C=O bond length of 1.16 Å, with an O=C=O bond angle of 180.0 degrees. The N₂ 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 N₂ molecule was assigned a negative charge on each N atom, that is, $q_N = -0.482 e$, and a positive charge at the COM site, that is, $q_{COM} = 0.964 e$.²¹ The H₂O molecule was simulated using the TIP3P model,²² which is a three-site rigid model that accounts for its intrinsic dipole moment. The partial charges on H and O atoms are $q_H = 0.417 e$ and $q_O = -0.834 e$, 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.²³ As shown in Table 1, the LJ parameters for the other species

Table 1. Potential Parameters for Force Field Calculations

		ϵ_{ff}/k_B [K]	σ_{ff} [Å]
TraPPE ¹⁹	C(CO ₂)	27	2.8
	O(CO ₂)	79	3.05
1CLJ ¹⁹	CH ₄	148	3.75
TraPPE ²¹	N(N ₂)	36	3.31
	COM(N ₂)		
TIP3P ²²	H(H ₂ O)		
	O(H ₂ O)	76.58	3.15
C(graphite)		28	3.4
O(surface functional groups) ²⁴		79	3.1
H(surface functional groups) ²⁴		30	1.31

contained within the surface functional groups were taken from previous molecular simulation studies of Tenney and Lastoskie,²⁴ where ϵ_{ff}/k_B is the depth of the potential well, σ_{ff} is the finite distance at which the interparticle potential is zero. The CO₂–CO₂ interactions and the interactions between CO₂/CH₄/N₂ 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 LJ 12–6 potential, with the electrostatic interactions calculated based on 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 ϵ and σ at the various LJ sites of the functional groups, including a more accurate σ 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 H₂O molecules.

2.3. Molecular Simulations. Grand canonical Monte Carlo (GCMC) simulations²⁵ of CO₂ adsorption in idealized organic microporous carbons were carried out in the μVT ensemble.²⁶ In the current work, to focus on the effect of the surface functionalities and the selectivity of CO₂ from CO₂/N₂ and CO₂/CH₄ 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

equation of state.²⁷ 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,¹ 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

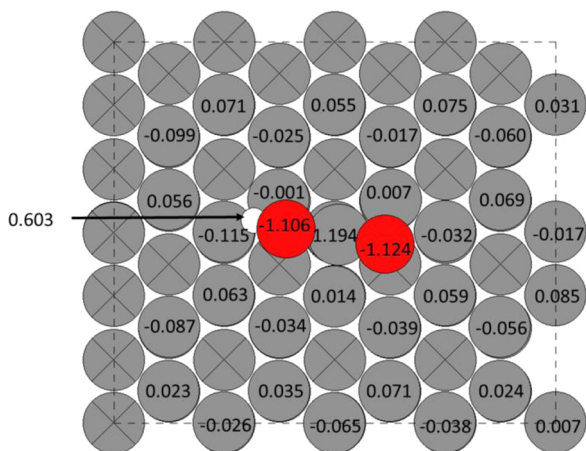


Figure 2. Partial charge distribution of carboxyl embedded graphitic surface. Gray, carbon atoms (cross represents bottom two layers); red, oxygen atom.

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.¹ 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.¹

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,²⁸ 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 2. Effect of Surface Functionality on the Adsorption of Gas Species in the Equimolar Mixtures at $T = 298$ K

			PG	OX	OH	C=O	C=O_COH	COH_C=O	COOH	MonoV
CO ₂ /CH ₄ (300 bar)	CO ₂	density [mmol/cm ³]	11.67	16.86	18.13	18.10	18.11	17.55	18.19	10.63
		increase percentage [%]		44	55	55	55	50	56	−9
	CH ₄	density [mmol/cm ³]	7.06	4.26	4.34	4.13	3.87	4.53	3.52	7.68
		increase percentage [%]		−40	−39	−42	−45	−36	−50	9
CO ₂ /N ₂ (150 bar)	CO ₂	density [mmol/cm ³]	15.09	18.76	20.32	20.10	20.00	20.37	20.14	15.33
		increase percentage [%]		24	35	33	33	35	33	2
	N ₂	density [mmol/cm ³]	2.47	1.64	1.60	1.50	1.44	1.52	1.26	2.50
		increase percentage [%]		−34	−35	−39	−42	−38	−49	1

of surface functionalities on selective gas adsorption. As shown in Table 2, in the case of the CO₂/CH₄ mixture, the oxygen-containing functional groups lead to an increase in the density of adsorbed CO₂, especially in the case of carboxyl functionalized graphitic slit pores, in which the density is increased by approximately 56%. Meanwhile, the adsorbed CH₄ 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 CO₂ adsorption with enhanced CH₄ 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 CO₂ it will be preferentially attracted by negatively charged surface atoms, which causes an enhancement of CO₂ adsorption over CH₄ due to the nonpolarity of CH₄. This behavior is similar in the case of CO₂/N₂ mixtures at $p = 150$ bar, where N₂ has weaker polarity compared to that of CO₂.

To further explore the effect of surface functionality on the adsorption of gas mixtures, the selectivity of CO₂ from CO₂/CH₄ and CO₂/N₂ 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 CO₂ from the gas mixture is defined as follows:

$$S_{\text{CO}_2/\text{CH}_4} = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{y_{\text{CO}_2}/y_{\text{CH}_4}}, S_{\text{CO}_2/\text{N}_2} = \frac{x_{\text{CO}_2}/x_{\text{N}_2}}{y_{\text{CO}_2}/y_{\text{N}_2}} \quad (2)$$

such that S represents the selectivity of CO₂ of a gas mixture, x_{CO_2} is the molar fraction of CO₂ in the adsorbed phase, and y_{CO_2} represents the mole fraction of CO₂ in the bulk gas phase. In the current study, the mole fraction of CO₂ and other gas species (e.g., CH₄ or N₂) are both kept as 0.5, with an estimated selectivity greater than 1 indicating that CO₂ 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 CO₂ over CH₄ increases from approximately 2 to higher than 5, especially in the low-pressure region. The selectivity of CO₂ over CH₄ in a perfect graphite slit pore is consistent with the values reported by Heuchel et al.²⁹ and Nicholson,³⁰ which are in the range of 1–4 under similar conditions. Due to the induced polarity of a functionalized surface, CO₂ will always preferentially adsorb over CH₄ due to the quadrupole moment of CO₂ (i.e., -13.7×10^{-40} Coulomb·m²).² Tetrahedral molecule CH₄ 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 CO₂ over N₂ increases from approximately 5 to 20. The higher selectivity of CO₂ over N₂ compared to that of CO₂ over CH₄ is consistent with the research carried out by Heuchel et al.²⁹ and the experimental adsorption measurements of gas mixtures in coal by Hall et al.³¹ The quadrupole moment of N₂ is -4.9×10^{-40} Coulomb·m²,² which is lower than that of CO₂. Therefore, CO₂ preferentially adsorbs over N₂ to the functionalized surfaces due to the stronger polarity.

In addition to the investigation of mixtures including N₂ and CH₄, the existence of water vapor was also considered. As water vapor is present in flue gas at an approximate 10% concentration compared with CO₂ at ~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 CO₂ 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 CO₂ to these surfaces. As an example, the selectivities of CO₂ over water vapor were compared at 333 K and 1 bar, which is relevant to flue gas conditions.³² The selectivity is above 1 when the gas mixture is adsorbed on perfect graphite

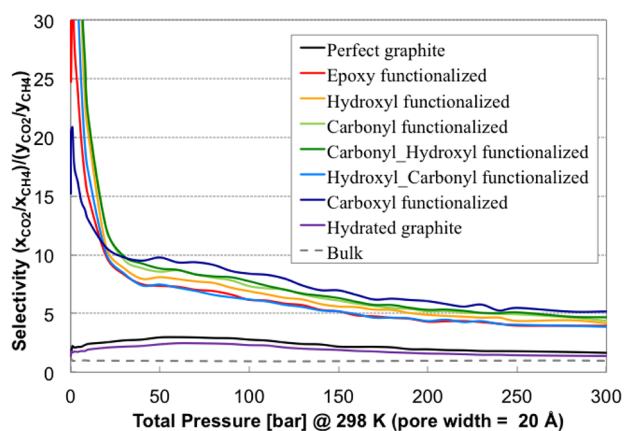


Figure 3. Selectivity of CO₂ over CH₄ from the CO₂/CH₄ mixture in slit pores with different embedded surface functional groups.

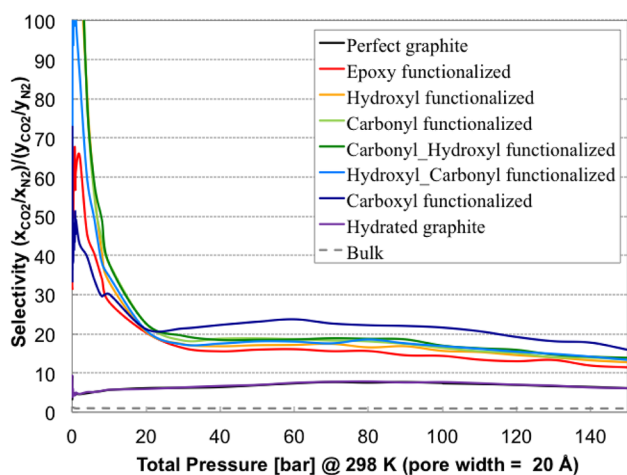


Figure 4. Selectivity of CO₂ over N₂ from the CO₂/N₂ mixture in slit pores with different embedded surface functional groups.

Table 3. Effect of Surface Functionality on the Selectivity of CO₂ from CO₂/H₂O Mixture

functional group	density of adsorbed CO ₂ (mmol/cm ³)	density of adsorbed H ₂ O (mmol/cm ³)	selectivity
perfect graphite	0.19	0.026	7.2124
epoxy functionalized	0.01	50.25	0.0002
hydroxyl functionalized	0.002	55.56	0.0000
hydrated graphite	2.86	0.34	8.5352

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

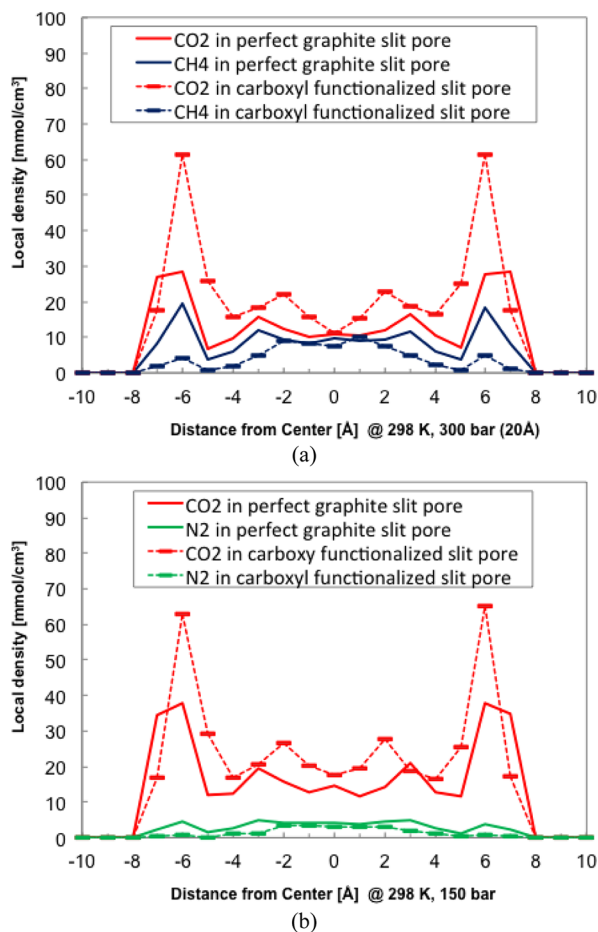


Figure 5. Comparisons of local density distribution of different gas species in the carboxyl functionalized micropores with that in the perfect graphite slit pore with pore width of 20 Å. (a) Mixture of CO₂ and CH₄; (b) Mixture of CO₂ and N₂.

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

The authors declare no competing financial interest.

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REFERENCES

- (1) Liu, Y.; Wilcox, J. Effects of surface heterogeneity on the adsorption of CO₂ in microporous carbons. *Environ. Sci. Technol.* **2012**, *46*, 1940–1947.
- (2) Wilcox, J. *Carbon Capture*; Springer Publishing: New York, 2012.
- (3) Benson, S.; Cook, P. *Intergovernmental Panel on Climate Change, Special Report on Carbon dioxide Capture and Storage: Underground geological storage*; University Press: Cambridge, UK, 2005; Ch. 5, 196–276.
- (4) White, C. M.; Smith, D. H.; Jones, K. L.; Goodman, A. L.; Jikich, S. A.; LaCount, R. B.; et al. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery—A review. *Energy Fuels* **2005**, *19*, 659–724.
- (5) Jorge, M.; Seaton, N. A. Predicting adsorption of water/organic mixtures using molecular simulation. *AIChE J.* **2003**, *49* (8), 2059–2070.
- (6) Shevade, A. V.; Jiang, S.; Gubbins, K. E. Adsorption of water-methanol mixtures in carbon and aluminosilicate pores: a molecular simulation study. *Mol. Phys.* **1999**, *97* (10), 1139–1148.
- (7) Shevade, A. V.; Jiang, S.; Gubbins, K. E. Molecular simulation of water-methanol mixtures in activated carbon pores: A molecular simulation study. *J. Chem. Phys.* **2000**, *113*, 6933–6942.
- (8) Nicholson, D.; Gubbins, K. E. Separation of carbon dioxide - methane mixtures by adsorption: Effects of geometry and energetics on selectivity. *J. Chem. Phys.* **1996**, *104*, 8126–8134.
- (9) Kurniawan, Y.; Bhatia, S. K.; Rudolph, V. Simulation of binary mixture adsorption of methane and CO₂ at supercritical conditions in carbons. *AIChE J.* **2006**, *52* (3), 957–967.
- (10) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.
- (11) Van Krevelen, D. W. *Coal*, 3rd completely revised ed.; Elsevier, Amsterdam, The Netherlands, 1991.
- (12) Kresse, G.; Furthmüller, J. Efficiency of ab initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (13) Kresse, G.; Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* **1993**, *48*, 13115–13118.
- (14) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (15) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*.
- (16) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (17) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (18) Yang, R. T. *Gas Separation by Adsorption Processes*; Imperial College Press: London, 1997.
- (19) Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. I. United-atom description of *n*-alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577.
- (20) Potoff, J.; Siepmann, J. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide and nitrogen. *AIChE J.* **2001**, *47*, 1676–1682.
- (21) Murthy, C. S.; Singer, K.; Klein, M. L.; McDonald, I. R. Pairwise additive effective potentials for nitrogen. *Mol. Phys.* **1980**, *41* (6), 1387–1399.
- (22) Jorgensen, W. L. Revised TIP3P for simulations of liquid water and aqueous solutions. *J. Chem. Phys.* **1982**, *77*, 4156.
- (23) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press, 1989.
- (24) Tenney, C. M.; Lastoskie, C. M. Molecular simulation of carbon dioxide adsorption in chemically and structurally heterogeneous porous carbons. *Environ. Prog.* **2006**, *25* (4), 343–354.
- (25) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*, 2nd ed.; Academic Press: New York, 2001.
- (26) Gupta, A.; Chempath, S.; Sanborn, M. J.; Clark, L. A.; Snurr, R. Q. Object-oriented programming paradigms for molecular modeling. *Mol. Simul.* **2003**, *1* (29), 29–46.
- (27) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill Book Company, 1987.
- (28) Sing, K. S. W.; Everett, et al. *Reporting Physisorption Data for Gas/Solid Systems., Handbook of Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- (29) Heuchel, M.; Davies, G. M.; Buss, E.; Seaton, N. A. Adsorption of carbon dioxide and methane and their mixtures on an activated carbon: Simulation and experiment. *Langmuir* **1999**, *15* (25), 8695–8705.
- (30) Nicholson, D. A simulation study of energetic and structural heterogeneity in slit-shaped pores. *Langmuir* **1999**, *15* (7), 2508–2515.
- (31) Hall F. E., Zhou C. H., Gasem K., Robinson Jr. R. L., Yee D. Adsorption of Pure methane, nitrogen, and carbon dioxide and their binary mixtures on wet Fruitland coal. Paper SPE 29194 presented at Eastern Regional Conference and Exhibition held at Charleston, WV, U.S.A. on November 8–10, 1994.
- (32) Sjöström, S.; Krutka, H. Evaluation of solid sorbents as a retrofit technology for CO₂ capture. *Fuel* **2010**, *89* (6), 1298–1306.
- (33) Bae, Y.-S.; Farha, O. K.; Hupp, J. T.; Snurr, R. Enhancement of CO₂/N₂ selectivity in a metal-organic framework by cavity modification. *J. Mater. Chem.* **2009**, *19*, 2131–2134.
- (34) Liu, B.; Smit, B. Comparative molecular simulation study of CO₂/N₂ and CH₄/N₂ separation in zeolites and metal-organic frameworks. *Langmuir* **2009**, *25* (10), 5918–5926.