Synergetic effect of carbon nanopore size and surface oxidation on CO\textsubscript{2} capture from CO\textsubscript{2}/CH\textsubscript{4} mixtures

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\textbf{A B S T R A C T}

We have studied the synergetic effect of confinement (carbon nanopore size) and surface chemistry (the number of carbonyl groups) on CO\textsubscript{2} capture from its mixtures with CH\textsubscript{4} at typical operating conditions for industrial adsorptive separation (298 K and compressed CO\textsubscript{2}/CH\textsubscript{4} mixtures). Although both confinement and surface oxidation have an impact on the efficiency of CO\textsubscript{2}/CH\textsubscript{4} adsorptive separation at thermodynamics equilibrium, we show that surface functionalization is the most important factor in designing an efficient adsorbent for CO\textsubscript{2} capture. Systematic Monte Carlo simulations revealed that adsorption of CH\textsubscript{4} either pure or mixed with CO\textsubscript{2} on oxidized nanoporous carbons is only slightly increased by the presence of functional groups (surface dipoles). In contrast, adsorption of CO\textsubscript{2} is very sensitive to the number of carbonyl groups, which can be examined by a strong electric quadrupolar moment of CO\textsubscript{2}. Interestingly, the adsorbed amount of CH\textsubscript{4} is strongly affected by the presence of the co-adsorbed CO\textsubscript{2}. In contrast, the CO\textsubscript{2} uptake does not depend on the molar ratio of CH\textsubscript{4} in the bulk mixture. The optimal carbonaceous porous adsorbent used for CO\textsubscript{2} capture near ambient conditions should consist of narrow carbon nanopores with oxidized pore walls. Furthermore, the equilibrium separation factor was the greatest for CO\textsubscript{2}/CH\textsubscript{4} mixtures with a low CO\textsubscript{2} concentration. The maximum equilibrium separation factor of CO\textsubscript{2} over CH\textsubscript{4} of \textasciitilde 18–20 is theoretically predicted for strongly oxidized nanoporous carbons. Our findings call for a review of the standard uncharged model of carbonaceous materials used for the modeling of the adsorption separation processes of gas mixtures containing CO\textsubscript{2} (and other molecules with strong electric quadrupolar moment or dipole moment).

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1. Introduction

The study of adsorption and separation of CO\textsubscript{2}/CH\textsubscript{4} mixtures on pure and oxidized nanoporous carbonaceous materials, near ambient operating conditions, is important from both fundamental and practical perspectives. From a fundamental perspective: the equilibrium adsorption and separation of molecules with large electric quadrupolar moments like CO\textsubscript{2} depends on two factors: the size/topology of carbon nanopores (i.e., effect of nanoscale confinement) and the specific short-range interactions with oxygen-containing functional groups dispersed on the carbon surface [1–15]. It is expected that specific dipole-quadrupolar interactions give rise to preferential adsorption of CO\textsubscript{2} over non- and weakly polar fluids (e.g., CH\textsubscript{4}, N\textsubscript{2}, SF\textsubscript{6}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, and others) at low pore loadings [13,14,16–28]. Furthermore, it is commonly known that an enhanced adsorption field in carbon nanopores increases CO\textsubscript{2} adsorption capacity and the equilibrium separation factor over the above-mentioned fluids at low pore loadings [5–10,15,29–35]. However, it is not clear how various factors including bulk mixture composition, pore loading, the number and type of surface oxygen-containing groups, and carbon texture impact on the CO\textsubscript{2}/CH\textsubscript{4} separation factor near ambient operating conditions. From a practical perspective, developing methods to energy efficient capture of CO\textsubscript{2} from industrial combustion exhaust gases is a challenge with enormous environmental implications. Optimization of the CO\textsubscript{2}/CH\textsubscript{4} separation factor is also crucial for practical implementation of novel solutions in clean energy technologies, such as coalbed methane recovery, geologic CO\textsubscript{2} sequestration, shale gas exploration, and others [15,36–42].

Oxygen is chemically bound to the carbon surface in the course of oxidation [43–47]. Unsaturated carbon edges are oxidized by exposure to air at room temperature. This phenomenon, called "aging", depends on the relative humidity, temperature, and the reactivity/topology of carbonaceous material. Therefore, no pure carbonaceous material exists, but carbon surface becomes more and more oxidized (i.e., hydrophilic) with time. It is to be expected that most of oxygen is bounded by covalent bounds in the form of
oxygen-containing functional groups, such as carboxyl, phenolic hydroxyl, carboxyl, carboxylic anhydrides, lactones, lactols, and ether-type oxygen atoms [43–45,48,49]. Obviously, one can easily adjust the number and chemistry of the oxygen-containing functional groups on carbon surface by controlled oxidation processes. Concentrated nitric acid, perhydrol, and potassium permanganate are the most common oxidation agents [45,48,50–53].

The impact of carbon oxidation on adsorption and separation of non- and weakly polar fluids from the gas phase is poorly understood. Tamon and Okazaki [54] investigated the influence of acidic surface oxides of activated carbon on gas adsorption characteristics. They showed that mild oxidation of a microporous CAL activated carbon (Calgon Co. Ltd., USA) sample by HNO3 slightly reduces micropore volume and surface area. Moreover, the oxidation of micro- and nanoporous carbonaceous materials by exposure to air at room temperature is not expected to impact on the surface topology and porosity of carbonaceous materials. In common with others, Tamon and Okazaki [54] found that during adsorption of water and ammonia from gas phase, adsorption capacity increases greatly with oxidation of carbon sample. Furthermore, ammonia was irreversibly adsorbed on oxidized carbon samples. Interestingly, the adsorption isotherms of simple alcohols (i.e., CH3OH, C2H5OH, and others); C6H5OH, and C6H12 on pure and oxidized carbon samples were almost identical. Thus, this experiment shows that the presence of the specific short-range interactions between some polar molecules and oxygen-containing functional groups does not necessarily increase their adsorption. Cluster formation around oxygen-containing functional groups is a possible explanation of these experimental findings. In contrast to water, the clustering of other polar molecules around charged O–C dipole is expected to be much weaker. First, these polar molecules are larger than water. The packing at restricted nanospaces may inhibit the accessibility of functional group to clusters composed of larger polar molecules. Second, the strength of hydrogen bonds (H-bonds) formed by other polar molecules is much weaker as compared to water. Because the clusters of polar molecules are too small, they do not aggregate at higher vapor pressures. Thus, the adsorbed amount is not enhanced by the cluster-mediated mechanism of adsorption that is responsible for high water uptake. What about adsorption of CO2 on pure and oxidized carbonaceous materials? From the electronic properties, it is expected that large electric quadrupolar moment of CO2 (i.e., 13.4 \times 10^{-40} \text{C m}^2) will develop the specific short-range directional interactions with the oxygen-containing functional groups [13,14,16–28]. Therefore, at low pore loadings, the equilibrium CO2/CH4 separation factor should increase with the content of the surface oxygen. However, two important questions arise. First, how much will the CO2/CH4 separation efficiency increase with surface oxidation? Second, how will the CO2/CH4 separation efficiency on pure and oxidized carbonaceous materials depend on the pore size and bulk/pore mixture composition?

In contrast to surface chemistry, the impact of the pore size on the adsorption and separation of CO2 from gas mixtures by nanoporous carbonaceous materials has been explored and understood. Recently, Sevilla and Fuertes [55] have summarized the CO2 adsorption capacities for various carbonaceous materials measured at 298 K and 1 bar. As expected, CO2 adsorption capacity is strongly correlated with the content of narrow carbon nano- and micropores. Activated graphite fibers and mesoporous carbons absorb only 1.3–1.7 mmol/g (storage per mass: 59–76 mg/g). In contrast, highly microporous sustainable porous carbon samples prepared by chemical activation of hydrothermally carbonized polysaccharides and biomass are able to adsorb 5.5–5.8 mmol/g (storage per mass: 230–256 mg/g). Furthermore, these porous carbons exhibit a high CO2 adsorption rate, a good selectivity for CO2/N2 separation and can be easily prepared. Silvestre-Albero et al. [56] reported similar high CO2 adsorption uptake in microporous carbon samples produced by the chemical activation of petroleum pitch (i.e., 4.7 mmol/g, storage per mass: 207 mmol/g at 293 K and 1 bar). Finally, Builes et al. [57] investigated the CO2 uptake in two samples of novel microporous zeolite template carbons (i.e., EMT-ZTC and FAU-ZTC). Both carbon samples adsorbed exceptionally high amount of CO2 at higher pressures, \( \sim 30–35 \text{ mmol/g} \) at 273 K and 30 bar. It is worth pointing out that these CO2 adsorption capacities are competitive with the best organic and inorganic adsorbing frameworks (zeolites and mesoporous silicas, COFs and MOFs). Taking into account experimental and recent theoretical results obtained by Palmer et al. [10] and Kowalczyk et al. [58], it seems reasonable to assume that carbonaceous materials with a large number of narrow carbon nanopores (pore size \( \sim 0.5–0.6 \text{ nm} \)) are optimal for CO2 adsorption. In strong confinement imposed by carbon nanopores, the linear shaped CO2 molecules have broken rotational symmetry. Highly oriented adsorbed CO2 molecules maximize their dispersion interactions with carbon pore walls. Moreover, as has been also shown, the equilibrium separation factor of CO2 over other simple molecules is also very high in narrow carbon nanopores [6,29]. Nevertheless, we need to take care to the conclusions that have been taken from experimental results. This is because the experimental samples of carbonaceous materials are never pure carbon. They inherently possess some surface functional groups, defect, heteroatoms, mineral contaminants, etc. Therefore, it is hard or even impossible to isolate the impact of porosity and surface oxidation on the CO2 adsorption and separation from the raw experimental measurements. Computer simulation studies are powerful methods that complement and extrapolate experimental knowledge.

In the current work, we study the cooperative effect of the structural heterogeneity (i.e., distribution of nanopore sizes) and surface oxidation on the equilibrium of CO2/CH4 mixture adsorption and separation at 298 K. For this purpose, we systematically investigated CO2/CH4 single-component and mixture adsorption on a series of well-defined pure/oxidized virtual porous carbon samples (VPCs) at various operating conditions, including the entire range of CO2 molar fractions in the bulk mixture. Most of the experimental studies in the literature focus on either the impact of porosity or the surface chemistry on CO2 capture by adsorption. On the other hand, simulation studies have been limited to pure carbonaceous materials that are poor approximation to these used in industrial separation processes. Therefore, in the current work, we concentrated on two major issues. First, we used Monte Carlo simulations to advance our understanding at the microscopic level of the adsorption mechanism of CO2/CH4 mixtures on pure/oxidized carbonaceous materials at industrial operating conditions. Second, we predicted theoretically the maximum equilibrium separation factor of CO2 over CH4 on pure/oxidized carbonaceous materials at 298 K. We believe that presented results are not limited to carbonaceous materials, and they are viable information for designing of efficient adsorbents for the equilibrium CO2/CH4 mixture separation.

2. Calculation details

2.1. Simulation boxes

The S00 virtual porous carbon (VPC) sample proposed by Harris et al. [59,60] was used to generate a sequence of VPCs samples with different porosities. This sequence was obtained by randomly placing subsequent small carbon fragments in pores of the S00 VPC sample [60]. Therefore, the pore size distributions of generated VPCs were progressively shifted to narrower carbon nanopores. Subsequent VPCs samples were denoted respectively as S00, S04,
study the equilibrium CO₂/CH₄ mixture adsorption/separation at 298 K [63–65]. We investigated four values of the total CO₂/CH₄ mixture pressure. To make the study relevant to industrial conditions (298 K and compressed CO₂—CH₄ mixtures), we selected atmospheric pressure (0.1 MPa) and three higher pressures, that is, 0.25, 0.5, and 1.0 MPa, respectively. For each total pressure, we studied the following CO₂ mole fractions in bulk phase (y_{CO₂}): 0.0, 0.01, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.975, 0.99, and 1.0. In our GCMC simulations, the previous configuration of adsorbed mixture was updated by the randomly selected perturbation: (i) displacement and/or rotation of randomly chosen molecule, (ii) creation of new molecule, (iii) annihilation of randomly chosen existing molecule, or (iv) swap move with equal probabilities. We used equal probability for each perturbation to guarantee the condition of microscopic reversibility. Each GCMC simulation run consisted of 2.5 × 10⁸ iterations. The first 1.0 × 10⁸ iterations were discarded to guarantee equilibration.

As previously, we used the rigid model for both CO₂ and CH₄ molecules [13,66,67]. The three-site model with force field developed by Nguyen was used for CO₂ [68]. For CH₄, we used the revised five-site model proposed by Sun et al. [66]. The values of the parameters for the carbonaceous skeleton and the atoms forming carbonyl groups were taken from our previous studies [13,14,69]. Table 1 collects all applied values of the interaction parameters. The Lorentz–Berthelot mixing rules were used for calculation of cross-term energy parameters. Other computations details are documented in our previous works [13,66]. Note that in our simulation model, the CO₂-carbonyl group interactions are treated as pure electrostatic ones. The possibility of partial charge transfer between CO₂ and carbonyl group (i.e., Lewis acid–base reaction) was excluded because of high thermal energy and constraints imposed by carbonaceous matrix.

From GCMC simulations, we determined the average numbers of CO₂ and CH₄ in the simulation box (i.e., (CO₂) and (CH₄)). Then, the mole fraction of CO₂ and CH₄ in the adsorbed phase is simply given by:

\[ x_{CO₂} = \frac{(CO₂)}{(CO₂) + (CH₄)} \] (1)

\[ x_{CH₄} = \frac{(CH₄)}{(CO₂) + (CH₄)} \] (2)

The equilibrium separation factor of CO₂ over CH₄ is computed from well-known relation [64]:

\[ S_{CO₂/CH₄} = \frac{x_{CO₂}}{x_{CH₄}} \frac{y_{CO₂}}{y_{CH₄}} \] (3)

where \( x \) and \( y \) are the mole fractions of the studied mixture components in adsorbed and bulk phase, respectively. The enrichment of adsorbed phase in CO₂ mixture component corresponds to \( S_{CO₂/CH₄} > 1 \).
3. Results and discussion

Knowledge of the pore size distribution of carbonaceous materials is one of the most important factors influencing the efficiency of adsorptive separation. Fig. 2 shows histograms of pore diameters computed for the studied VPCs. Taking into account the International Union of Pure and Applied Chemistry (IUPAC) classification of pores, all studied VPCs are microporous materials (i.e., pore diameters are less than 2 nm). As it was discussed in our previous study [60], passing from S00 to S35 sample, we notice a gradual increasing from the contribution of the smallest carbon nanopores. Further, as we added more and more carbon fragments to S00 VPC sample, the pore size distributions are more homogenous and shifted to smaller carbon nanopores. This is obvious since the

![Fig. 2. Comparison of the histograms of pore diameters (P(\(d_{eff}\))) and related integral curves (Pint(D) = \(\Sigma_{d_{eff}} P(d)\)) computed for all considered VPCs (histograms were recalculated with resolution of 0.05 nm and subsequent histograms were shifted from the previous ones by 0.11 in part (a), by 0.08 in part (b) and by 0.12 in part (c)).](image-url)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Geometric parameters</th>
<th>Centre</th>
<th>(\sigma) (nm)</th>
<th>(\epsilon/k_B) (K)</th>
<th>(q/e)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>(l_{C-O} = 0.1162) nm</td>
<td>C</td>
<td>0.2824</td>
<td>28.680</td>
<td>+0.664</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>0.3026</td>
<td>82.000</td>
<td>-0.332</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>(l_{C-H} = 0.1090) nm</td>
<td>C</td>
<td>0.3400</td>
<td>55.055</td>
<td>-0.660</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>0.2650</td>
<td>7.901</td>
<td>+0.165</td>
<td></td>
</tr>
<tr>
<td>VPC</td>
<td>(l_{C-O} = 0.1233) nm</td>
<td>C(^{c})</td>
<td>0.3025</td>
<td>30.600</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(^b)</td>
<td>0.3400</td>
<td>28.000</td>
<td>0.000</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>0.2960</td>
<td>105.800</td>
<td>-0.500</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Cross-interaction parameters.  
\(^b\) Non-carbonyl group atom of C.  
\(^c\) Carbonyl group C atom.
random addition of carbon fragments located in wider pores leads to creation of smaller pores. Contrary, the procedure of "virtual oxidation" practically does not change the PSD curve (Fig. 2b,c) since introduced, on the edges of carbon fragments, oxygen atoms occupy small volume in comparison with the volume of carbon fragments [13]. This observation is in good agreement with experiment [54], which further confirms the reliability of the virtual oxidation algorithm.

Figs. S1–S3 in Supplementary data depict CO$_2$ and CH$_4$ single-component adsorption isotherms computed from GCMC for all the studied VPCs samples. Here, we express the absolute value of adsorption as an average number of molecules in the simulation box. For comparison and further discussion of the simulation results, we express the absolute value of adsorption as an average number of molecules per unit mass adsorbent too. As would be expected, both porosity and oxygen content affect the adsorption of

Fig. 3. Variation of CO$_2$ mole fraction with composition and pressure of gaseous mixture computed for all studied VPCs. Dashed line corresponds to "x = y".
both CO₂ and CH₄ adsorbates. Interestingly, regardless of the porosity and oxidation intensity of studied VPCs, the CO₂ adsorption amount is at least two times greater than the CH₄ adsorption amount. Further, we notice that for both CO₂ and CH₄ narrowing of pore diameters results in higher number of adsorbed molecules in the simulation box. The region of high pressures is an exception. This is because the nanopore volume accessible for adsorbed molecules decreases after adding additional graphitic fragments to the initial S00 VPC sample (see upper panel in Fig. S1 in Supplementary data). As would be expected, the CO₂ and CH₄ adsorbed amount expressed per unit mass of adsorbent is decreasing with the narrowing of the pore diameters. A significant increase in the number of carbon atoms in the simulation box for VPCs samples characterized by the narrow nanoporosity is responsible for this effect (compare sample S00 and S35). Careful inspection of the simulation results revealed that the single-component CO₂ adsorption isotherms are more affected by porosity/surface oxidation than the single-component CH₄ ones. The increase in oxygen content causes an increase in the adsorbed amount.

Fig. 4. Variation of CO₂/CH₄ equilibrium separation factor with composition and pressure of gaseous mixture computed for all studied VPCs. The arrows show the direction of changes analogically as in Fig. 3.
increase in adsorption of both studied adsorbates. However, we notice that the presence of carbonyl functional groups affects the CO₂ uptake far more than CH₄ one (see Figs. S2 and S3 in Supplementary data). In the case of CH₄, the presence of oxygen-containing groups increases slightly adsorption, while the CO₂ uptake is increased by up to several tens of percent. Analogous effects were reported in our previous papers [13,14,67]. Observed regularities can be easily explained by the polar nature of studied adsorbates. CO₂ molecule has strong electric quadrupolar moment, while CH₄ has only weak electric octupolar moment. Therefore, the electrostatic interactions of CO₂ with carbonyl groups (which are dipoles) are far stronger and slowly decrease with the intermolecular distance in the comparison with CH₄ [70].

For clarity of the presented simulation results, for all studied CO₂/CH₄ mixtures, we express the adsorption amount of mixture components as an average number of molecules in the simulation box. Clearly, one should expect that the electrostatic interactions play an essential role in a case of CO₂/CH₄ mixture adsorption and separation. However, we need bear in mind that co-adsorption and displacement of mixture components from carbon nanopores are also affected by their mutual interactions (particularly at high pore loadings). Figs. 3 and 4 display the variation of the CO₂ mole fraction and equilibrium separation factor as a function of the CO₂ mole fraction in the bulk mixture. Additionally, Figs. S4–S6 in Supplementary data present the comparison between the average number of CO₂ and CH₄ molecules in simulation boxes. We notice that for all studied VPCs samples, the CO₂ mole fraction in the adsorbed phase (yCO₂) is significantly higher than in the gaseous phase (yCO₂). This is because CO₂ molecules are preferentially adsorbed over CH₄ ones. Furthermore, the equilibrium separation factor is monotonically decreasing with the concentration of CO₂ in the bulk mixture. This monotonic reduction in the equilibrium separation factor is strongly marked for low and moderate CO₂/CH₄ total mixture pressures. Here, we predicted that CO₂/CH₄ mixtures with dilute CO₂ mixture component can be efficiently separated by studied VPCs materials. Interestingly, for high total CO₂/CH₄ mixture pressures, we predicted a non-monotonic variation of the equilibrium separation factor with the CO₂ concentration in the bulk mixture. Here, equilibrium separation factor is higher for high CO₂ concentration in the bulk mixture as compared to its infinite dilution. Therefore, we suggest that the CO₂/CH₄ mixtures can be also efficiently purified by adsorption at high operating pressures. The energy consumption of high-pressure adsorptive separation favors the CO₂/CH₄ mixtures with low CO₂ concentration.

Let us now analyze the CO₂/CH₄ mixture adsorption on pure VPCs in details (i.e., S00–S35, see Figs. 3a and 4a). Generally, the effect of pore size on pure VPC samples has a moderate effect on the equilibrium separation factor. Regardless of the total pressure and mixture composition, the CO₂ mole fraction increases with narrowing of the pore diameters (i.e., from S00 sample to S35 one). This is why we observe an enhancement of the equilibrium separation factor by 1–2 for VPCs samples consisting the significant fraction of narrow carbon nanopores. Interestingly, the strongest effect is observed for the total CO₂/CH₄ mixture pressure of 1 MPa. Here, for all VPCs samples, the variation of equilibrium separation factor with the CO₂ concentration in the bulk mixture is non-monotonic, with initial decreasing and further increasing with CO₂ mole fraction in the bulk phase. Similar behavior (but weakly marked) is also observed for lower total pressure in the case of more nanoporous VPCs. This interesting result can be explained by the displacement of CH₄ from nanopores by co-adsorbed CO₂ molecules. As we have shown recently, the displacement of CH₄ from adsorbed phase by co-adsorbed CO₂ is facilitated in narrow carbon nanopores [15].

The presence of surface functionalities (i.e., oxygen-containing functional groups) has a far more important effect on the equilibrium CO₂/CH₄ separation factor than the porosity (see Figs. 3b–c and 4b–c). Increasing the oxygen content in VPCs results in substantial enhancement of the CO₂ mole fraction in the adsorbed phase. Therefore, the most oxidized VPCs samples (i.e., S00_180 and S35_360) show the equilibrium separation factor of 2–3 times greater than the pure VPCs ones. In the case of the S00_180 structure (having carbon nanopores dispersed in the range up to 2 nm), the equilibrium separation factors approach 8–10, while in the case of strictly nanoporous S35_360 VPC sample (having carbon nanopores with pore diameters below 1 nm), the values of equilibrium separation factor are ~2 times greater. This is a clear manifestation of the synergistic effect of the porosity and the surface oxidation on the energetic of CO₂ adsorption (see Fig. 5). As previously, at high total CO₂/CH₄ mixture pressures, we found higher equilibrium separation factor as compared to CO₂ infinite dilution.

![Fig. 5. Equilibrium snapshots of CO₂—CH₄ mixture adsorbed at 298 K on pure (upper panels) and maximally oxidized S35 (bottom panels) carbon sample. Studied CO₂ mole fractions (i.e., 0.1, 0.5, and 0.9) are displayed on the plot.](image-url)
Fig. 6. Variation of CO₂ (CH₄) absolute value of adsorption with CO₂ and CH₄ partial pressure computed for pure and selected oxidized S00 VPCs. For comparison, solid lines display the absolute value of adsorption corresponding to single-component adsorption.

Fig. 7. As in Fig. 6 but for selected VPCs based on S35 structure.
This is a consequence of CH$_4$ displacement from carbon nanopores and the co-adsorption of the CO$_2$ in the whole accessible pore volume. The comparison between the number of CO$_2$ molecules adsorbed in pure and oxidized VPCs samples clearly shows that oxidized carbonaceous materials adsorb more CO$_2$ at the same operating conditions (see Fig. 5 and Figs. S4–S6 in Supplementary data). In contrast, for CH$_4$, the number of adsorbed molecules is only slightly affected by the presence of the carbonyl groups.

Figs. 6 and 7 depict the partial pressure variation in the average number of adsorbed CO$_2$ and CH$_4$ molecules for selected samples of VPCs. Adsorption data computed for pure mixture components are also presented. We have grouped all simulation results in series corresponding to different values of total CO$_2$/CH$_4$ mixture pressure. It is clear that the presence of CH$_4$ has almost no influence on CO$_2$ adsorption from CO$_2$/CH$_4$ mixtures. More importantly, this conclusion seems to be correct for different mole fractions of CH$_4$ in the bulk phase. On the other hand, the presence of CO$_2$ in the bulk phase (even at low concentrations) strongly affects CH$_4$ adsorption. Note that this interesting observation is predicted for both pure and oxidized VPCs samples. In fact, it has been shown experimentally that to maximize the CO$_2$/X equilibrium separation factor (X denotes other component, such as CH$_4$ and N$_2$), one needs only to optimize the structure of porous materials with respect to CO$_2$ adsorption. Our simulation results give deeper understanding of this important feature of adsorptive CO$_2$/X mixture separation.

Concluding, we have shown that CO$_2$ is preferentially adsorbed over CH$_4$ on both pure and oxidized VPCs samples. However, the preferential adsorption toward CO$_2$ is intensified by the decrease in the average pore diameter and by the increase in surface oxidation. Therefore, in order to optimize the performance of activated carbons toward the equilibrium separation of CO$_2$/CH$_4$ mixtures, its pore size should be decreased, and the concentration of oxygen-containing functionalities should be increased. We argue that this conclusion is not limited to CO$_2$ mixtures with CH$_4$, but it is more general. A similar trend is expected for adsorptive separation of CO$_2$/X mixtures (where X is characterized by weaker electrostatic and dispersion interactions with oxidized porous materials as compared to CO$_2$). It is worth pointing out that our theoretical results are fully consistent with the recent simulation work of Lithoxoos et al. [71]. How distribution of partial charges (i.e., topology of functional groups) affects the CO$_2$/CH$_4$ equilibrium separation factor? We will address this question in our future works.

4. Conclusions

We have presented a detailed study of CO$_2$/CH$_4$ mixture adsorption and separation at 298 K on pure and oxidized virtual porous carbons using grand canonical Monte Carlo simulations. To the best of our knowledge, this is the first comprehensive work, where the synergetic effect of carbon nanopore size and surface oxidation on CO$_2$ adsorptive separation has been described. We found that surface oxidation is a far more important factor than carbon nanoporosity in influencing the efficiency of CO$_2$/CH$_4$ mixture separation at thermodynamics equilibrium. This is because short-range electrostatic interactions between adsorbate and functional groups (surface dipoles) are much stronger for CO$_2$ as compared to CH$_4$. Therefore, both single-component and mixture adsorption of CO$_2$ is significantly enhanced by the presence of surface functionalities. Furthermore, we have shown that the adsorbed amount of CH$_4$ is strongly affected by the presence of the co-adsorbed CO$_2$. Interestingly, CO$_2$ uptake does not depend on the molar ratio of CH$_4$ in the bulk mixture. Thus, by maximizing of CO$_2$ uptake, one can predict the optimal adsorbent (i.e., its porosity and surface oxidation) as well as operating conditions for its adsorptive separation. As a rule of thumb one can assume that the optimal adsorbent for CO$_2$ capture by equilibrium adsorption mechanism should consist of narrow carbon nanopores decorated by oxygen-containing functional groups. Moreover, the optimal operating conditions for CO$_2$/CH$_4$ mixture separation correspond to low concentration of CO$_2$ in the bulk mixture. At these operating conditions, the high CO$_2$/CH$_4$ equilibrium separation factor results from preferential adsorption of CO$_2$ over CH$_4$ at the most energetic centers of an adsorbent (i.e., in narrow nanopores with oxidized pore walls). Efficient separation at high CO$_2$/CH$_4$ mixture pressures is an interesting option but it will require significant energy consumption. At higher CO$_2$/CH$_4$ mixture pressures, the enrichment of adsorbed phase in CO$_2$ component results from displacement of CH$_4$ from porous adsorbents by co-adsorbed CO$_2$. High CO$_2$/CH$_4$ equilibrium separation factor of ~18–20 at 298 K is theoretically predicted and associated with the strong oxidation of nanoporous carbonaceous materials. Large number of surface dipoles distributed randomly on carbon pore walls can significantly enhance the CO$_2$/CH$_4$ separation efficiency at thermodynamics equilibrium.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.01.044.

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