Displacement of Methane by Coadsorbed Carbon Dioxide Is Facilitated in Narrow Carbon Nanopores

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Supporting Information

ABSTRACT: By using simulation methods, we studied the adsorption of binary CO₂−CH₄ mixtures on various CH₄ preadsorbed carbonaceous materials (e.g., triply periodic carbon minimal surfaces, slit-shaped carbon micropores, and Harris’s virtual porous carbons) at 293 K. Regardless of the different micropore geometry, two-stage mechanism of CH₄ displacement from carbon nanospaces by coadsorbed CO₂ has been proposed. In the first stage, the coadsorbed CO₂ molecules induced the enhancement of CH₄ adsorbed amount. In the second stage, the stronger affinity of CO₂ to flat/curved graphitic surfaces as well as CO₂−CO₂ interactions cause the displacement of CH₄ molecules from carbonaceous materials. The operating conditions of CO₂-induced cleaning of the adsorbed phase from CH₄ mixture component strongly depend on the size of the carbon micropores, but, in general, the enhanced adsorption field in narrow carbon ultramicropores facilitates the nonreactive displacement of CH₄ by coadsorbed CO₂. This is because in narrow carbon ultramicropores the equilibrium CO₂/CH₄ selectivity (i.e., preferential adsorption toward CO₂) increased significantly. The adsorption field in wider micropores (i.e., the overall surface energy) for both CO₂ and CH₄ is very similar, which decreases the preferential CO₂ adsorption. This suppresses the displacement of CH₄ by coadsorbed CO₂ and assists further adsorption of CH₄ from the bulk mixture (i.e., CO₂/CH₄ mixing in adsorbed phase).

I. INTRODUCTION

Recent experimental studies of the competitive adsorption of CO₂ and CH₄ on coal seams have revealed that CO₂ molecules injected into carbonaceous pores displace preadsorbed CH₄ molecules, thereby offering an enhancement of CH₄ recovery.¹⁻³ This scenario, also known as enhanced coalbed methane recovery (ECBM),⁴⁻¹⁰ seems to be an attractive method to reduce the amount of anthropogenic CO₂. This is because the injection of CO₂ into methane-rich coal seams (or other geological formations, such as: depleted oil and gas fields, unmineable coal, etc.) seems to enhance CH₄ recovery by a factor of two to three times over that achieved in simple desorption by pressure drawdown.¹ Therefore, the cost of CO₂ sequestration can be offset by ECMB. Coal is a complex heterogeneous sedimentary organic rock made of fossilized plant material and incorporated inorganic matter.¹¹⁻¹³ The maceral compositions indicate the botanic precursors and depositional histories for a coal and are divided into three groups:¹¹ “vitrinite” (remains of various plant matter such as bark, stems, roots, etc.), “liptinite” (cuticles, spores, resin, and algal remains), and “inertinite” (oxidized plant material, fungal remains, fossilized char, coal, etc.). Various molecular representations for the structure of coal have been proposed.¹² However, it is commonly accepted that coal is a 3-D macromolecular network structure consisting of polyaromatic and alkyl-substituted aromatic units linked by covalent and noncovalent bonds (hydrogen bonds, van der Waals interactions, electrostatic interactions, and π−π interactions).¹² The number/type of functional groups attached to the macromolecular network, the amount of preadsorbed water, and the content of mineral ash strongly depend on the origin of the coal.¹¹⁻¹⁵ Notice, that even for the same mine the coal structure and adsorption properties depend on the depth (i.e., they are function of increased stress).

Therefore, it is necessary to simplify the complex structure of coal to gain some basic insight into its adsorption/elastic properties. Let us consider the porosity of coals. It is commonly known that coal is predominantly composed of carbonaceous micropores smaller than 2 nm in diameter and mesopores ranging between 2 and 50 nm, with micropores making the largest contribution into the adsorption capacity.¹⁶⁻¹⁸ Narrow carbonaceous micropores of irregular shapes and various topologies are partially/completely filled by guest molecules, such as CH₄ and higher molecular weight hydrocarbons. Those molecules are trapped in narrow micropores by the enhanced adsorption potential (i.e., surface forces). Therefore, to first
approximation carbonaceous materials are good candidates to study the adsorption/coadsorption properties of some coals, such as anthracite. Note that the carbon content in anthracite is between 92 and 98%.\textsuperscript{11} Although we acknowledge the importance of H\textsubscript{2}O sorption in coals and activated carbons,\textsuperscript{19–27} this effect is not considered in this article.

To gain some basic insight into the mechanism of nonreactive CH\textsubscript{4} displacement from small carbonaceous micropores upon injection of CO\textsubscript{2}, we focus on the adsorption of binary CO\textsubscript{2}–CH\textsubscript{4} mixtures on selected CH\textsubscript{4} preadsorbed carbonaceous materials, including: triply periodic carbon minimal surfaces (Schwarz’s Primitive and Schoen’s Gyroid carbon minimal surfaces),\textsuperscript{28–31} slit-shaped carbon micro pores,\textsuperscript{32–36} and Harris’s virtual porous carbons (VPCs)\textsuperscript{37–40} at 293 K. Intuitively, one should expect that CO\textsubscript{2} molecules gradually displace preadsorbed CH\textsubscript{4} ones from carbonaceous micropores. This is because both CO\textsubscript{2}–CO\textsubscript{2} interactions as well as the interactions of CO\textsubscript{2} molecules with flat/curved graphitic fragments (i.e., surface energy) are greater as compared with their CH\textsubscript{4} counterparts.\textsuperscript{1} Therefore, upon adsorption of the binary CO\textsubscript{2}–CH\textsubscript{4} mixtures on CH\textsubscript{4} preadsorbed carbonaceous materials, the composition of the binary mixture in micropores will be continuously enriched with CO\textsubscript{2} mixture component until the complete displacement of preadsorbed CH\textsubscript{4} molecules. Note that following to this generally accepted scenario an increase in the partial pressure of CO\textsubscript{2} in the bulk mixture should result in a monotonic decrease in the pore density of preadsorbed CH\textsubscript{4} fluid. The bulk mixture enriched with recovered CH\textsubscript{4} can then be used as a viable energy source.

The molecular simulations performed here help us to understand the general mechanism of the binary CO\textsubscript{2}–CH\textsubscript{4} mixture adsorption on CH\textsubscript{4} preadsorbed carbonaceous materials at 293 K. We would like to answer the following question: how the enhanced solid–fluid potential in narrow carbon micropores will impact the displacement of preadsorbed CH\textsubscript{4} upon coadsorsorption of CO\textsubscript{2}. It is important to point out that in our modeling we assumed fast equilibration between the bulk mixture and the carbonaceous material (i.e., we excluded any high-energetic kinetic barriers limiting the diffusion of mixture components from the bulk mixture to the micropores).

The real materials, including coals, do not always fulfill this condition.\textsuperscript{11} However, to the best of our knowledge, the microscopic mechanism of CH\textsubscript{4} displacement from fully accessible carbonaceous micropores upon CO\textsubscript{2} coadsorption has not been investigated so far, and this is the primary goal of the current work.

II. SIMULATION DETAILS

II.I. Potential Models: Fluid–Fluid Interactions. In the current work we used fully atomistic representation for CO\textsubscript{2} and CH\textsubscript{4}. In the atomistic simulations, we expressed the intermolecular potential between two molecules A and B as a sum of site–site terms\textsuperscript{41–44}

\[ U^{A,B}(q) = \sum_{i} \sum_{j} u_{ij}(r_{ij}^{A,B}) \]  

where the sum is taken over all sites i of the molecule A and the sites j of the molecule B, q ≡ \{r_{ij} – r_{ij}^A\} \_ij is the set of separations between each atom in the molecule A and each atom in the molecule B, r_{ij}^{A,B} \_ij is the distance between two sites i and j on the molecules A and B, respectively, and u_{ij}(r) denotes distance-dependent site–site interaction potential. Depending on the type of the site, u_{ij}(r) is given by a pairwise dispersion or electrostatic interaction energy. We assumed that the dispersion energy of interaction is given by the (12,6) Lennard-Jones equation\textsuperscript{41–44}

\[ u_{ij}^{A,B} = 4\varepsilon_{ij}^{A,B} \left( \frac{\sigma_{ij}^{A,B}}{r_{ij}} \right)^{12} - \frac{\varepsilon_{ij}^{A,B}}{r_{ij}^{A,B}} \]  

(2)

The parameters of the potential, that is, \sigma_{ij}^{A,B} and \varepsilon_{ij}^{A,B}, were taken from Tables 1 and 2.

Table 1. Lennard-Jones Parameters and Partial Charges for the Three-Site Carbon Dioxide Model\textsuperscript{41–44}

<table>
<thead>
<tr>
<th></th>
<th>( \sigma_{ij} (\text{Å}) )</th>
<th>( \varepsilon_{ij}/k_B ) (K)</th>
<th>( l_{CO} (\text{Å}) )</th>
<th>q (e)</th>
</tr>
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<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>C: 2.824</td>
<td>C: 28.68</td>
<td>1.162</td>
<td>O: –0.332</td>
</tr>
<tr>
<td>O</td>
<td>O: 3.026</td>
<td>O: 82.0</td>
<td>C: 0.664</td>
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</tr>
<tr>
<td>C–O</td>
<td>C–O: 2.925</td>
<td>C–O: 48.495</td>
<td></td>
<td></td>
</tr>
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</table>

\textsuperscript{a}C–O denotes LJ parameters obtained from Lorentz–Berthelot mixing rule.\textsuperscript{41,42} l_{CO} is the C=O bond length.

Table 2. Lennard-Jones Parameters and Partial Charges for the Five-Site Methane Model\textsuperscript{47–49}

<table>
<thead>
<tr>
<th></th>
<th>( \sigma_{ij} (\text{Å}) )</th>
<th>( \varepsilon_{ij}/k_B ) (K)</th>
<th>( l_{CH} (\text{Å}) )</th>
<th>q (e)</th>
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</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td>C: 3.4</td>
<td>C: 55.055</td>
<td>1.09</td>
<td>O: –0.66</td>
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<tr>
<td>H</td>
<td>H: 2.65</td>
<td>H: 7.901</td>
<td>C: 0.165</td>
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<tr>
<td>C–H</td>
<td>C–H: 3.025</td>
<td>C–H: 30.6</td>
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<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}C–H denotes LJ parameters fitted to experimental data. l_{CH} is the C–H bond length.

We modeled electrostatic force via the Coulomb law of electrostatic potential\textsuperscript{41–44}

\[ u_{ij}^{A,B} = \frac{1}{4\pi\varepsilon_0} \frac{q_i^A q_j^B}{r_{ij}^{A,B}} \]  

(3)

where \varepsilon_0 is the permittivity of free space (\varepsilon_0 = 8.85419 \times 10^{-12} \ 	ext{C}^2\text{N}^{-1}\text{m}^{-2}), q_i^A denotes the value of the point charge j on the molecule A, q_j^B denotes the value of the point charge j on the molecule B, and r_{ij}^{A,B} is the distance between two charges i and j on the molecules A and B, respectively. The values of the point charges were taken from Tables 1 and 2. The applied force fields were validated against known experimental data in a series of our previous works.\textsuperscript{35–47}

II.II. Carbonaceous Porous Materials: Solid–Fluid Interactions. Triply periodic carbon minimal surfaces as well as VPCs were modeled by fully atomistic representation. The structures of the unit cell for two studied carbonaceous triply minimal surfaces (see Figure 1), that is, Schwarz’s P-surface (P denotes primitive) and Schoen’s G-surface (G denotes gyroid), were taken from previous works.\textsuperscript{28–30} These stable periodic graphitic structures (known also as “Schwarzites”) with negative curvature analogous to zeolites were theoretically predicted in 1991. Energetic calculations showed that Schwarzites carbon structures are more stable than C\textsubscript{60} buckminsterfullerene. This stability comes from the fact that in the heptagonal or octagonal carbon rings there is very little mechanical strain, thus preserving the sp\textsuperscript{2}-like nature of graphite. The ordered channels and labyrinths of model Schwarzites structures are attractive for potential separation.
of fluid mixtures. Two samples of Harris’ VPCs (S00 and S24) were taken from our previous work,’37–39 (see Figures 1S–3S in the Supporting Information). The solid–fluid interactions were computed from eq 2 by summing all dispersion interactions between carbon atoms and Lennard-Jones dispersion sites of adsorbate molecules. Here we assumed that all studied carbonaceous materials are uncharged. As previously, for carbon atoms, we used (12,6) Lennard-Jones parameters from Steele’s work: σ = 0.34 nm, ε/κ = 28.0 K.48,49 (For details, see section IS in the Supporting Information.)

For calculation of solid–fluid potential in studied slit-shaped carbon micropores, we used structureless Steele’s 10–4–3 potential.’48,49 The total adsorbate-carbon potential is a superposition of potentials exerted by opposing pore walls

\[ U_A(q) = \sum_{i=1}^{M} [u_i(z_i^A) + u_i(H - z_i^A)] \]

where \( q \equiv \{x_i^A, H - x_i^A\}_{i=1,2,...,M} \) is the set of separations between each LJ dispersion site on molecule A and pore walls, \( M \) is the number of dispersion sites of the molecule A (for CO_2, \( M = 3 \), whereas for CH_4, \( M = 5 \)), \( H \) denotes the slit-shaped carbon pore width, and \( u_i(x) \) is modeled by the 10–4–3 potential.’48,49

\[ u_i(x) = 2\sigma_{di}^6\varepsilon_{di}^{\sigma_{di}} \left[ \frac{2}{5} \frac{\sigma_{di}^6}{x^6} - \left( \frac{\sigma_{di}^6}{x^6} \right)^{5/2} \right] \]

\[ - \left( \frac{3\Delta(x + 0.61\Delta)^3}{\Delta(x + 0.61\Delta)^3} \right) \]

where \( \rho_i = 114 \text{ nm}^{-3} \) is the density of carbon atoms, \( \Delta = 0.335 \text{ nm} \) denotes the distance between carbon planes in graphite, and \( \sigma_{di} \) and \( \varepsilon_{di} \) denote LJ solid–fluid collision diameter and well depth, respectively. For all studied carbonaceous materials, the solid–fluid Lennard-Jones parameters were computed from Lorentz–Berthelot mixing rule.’41,42 (For details, see section IS attached to the Supporting Information.)

II.III. Simulation Protocol. Our computer experiment is schematically presented in Figure 2. We used Monte Carlo simulations in grand canonical ensemble (GCMC)’41,42 implemented to mimic the displacement experiment. First, we preadsorbed CH_4 molecules in micropores of the studied carbonaceous materials. The assumed partial pressure of CH_4 mixture component in the bulk phase controls the amount of preadsorbed CH_4. Next, we inject a small amount of CO_2 into bulk CH_4 and equilibrate the resulting mixture in contact with the studied porous carbonaceous material (see Figure 2). Note that the binary CO_2–CH_4 mixture is not in direct contact with carbonaceous material. Instead, the correct equilibrium composition of adsorbed phase is guaranteed by the Metropolis GCMC moves.’41,42 After equilibration, the composition of the adsorbed mixture is further recorded and analyzed. Note that gradually increasing the partial CO_2 pressure in the bulk mixture makes it possible to study the microscopic mechanism of CH_4 displacement from studied representative carbonaceous materials.

All studied carbonaceous materials were kept rigid during all computer experiments in the GCMC. This simplification is reasonable because we investigated the equilibrium properties of adsorbed mixtures. For triply periodic carbon minimal surfaces and VPCs, we imposed periodic boundary conditions along \( x, y, \) and \( z \) directions. As others,’50 for slit-shaped carbon micropores, we used two periodic dimensions (\( x \) and \( y \)). In all computer experiments, CO_2 and CH_4 molecules were kept rigid. This is because the applied force-field parameters were adjusted to rigid model of CO_2 and CH_4.’47,51 The Monte Carlo steps (in our simulations) consist of a grand canonical (Widom) insertion/deletion move and of a translational/rotation move. The details of these moves can be found elsewhere.’41,42,50 To attain microscopic reversibility and detailed balance, the translation/insertion/deletion move was selected with equal probability of 1/3. In each GCMC step, the mixture component was selected with equal probability. In all GCMC simulations, \( 10^8 \) configurations were used, of which we discarded the first \( 5 \times 10^7 \) to guarantee equilibration. The stability of the simulation results was confirmed by additional longer runs of \( 5 \times 10^8 \) configurations. Absolute value of adsorption (i.e., pore density) and potential energy was...
computed using energy/particle fluctuations in grand canonical ensemble.\textsuperscript{50}

III. RESULTS AND DISCUSSION

We begin our analysis by studying the microscopic mechanism of the binary CO\textsubscript{2}−CH\textsubscript{4} mixture adsorption on preadsorbed CH\textsubscript{4} triply periodic carbon minimal surfaces. Note that these carbonaceous materials are a good representation of ordered porous carbons. In fact, Schoen’s G carbon surface predicted theoretically in 1991\textsuperscript{30} has been already synthesized.\textsuperscript{52} Curved minimal carbon surfaces were also found in low-density carbonaceous materials such as glassy carbons.\textsuperscript{53} Surprisingly, for both P and G carbon minimal surfaces, we found a nonmonotonic relation between the partial pressure of CO\textsubscript{2} in the bulk mixture and the adsorbed amount of CH\textsubscript{4}. Let us analyze in detail the results displayed in Figures 3 and 4. If the partial pressure of CO\textsubscript{2} in the bulk mixture is negligible, then the amount of preadsorbed CH\textsubscript{4} is constant. Obviously, we get more preadsorbed CH\textsubscript{4} if its partial pressure in the bulk mixture is higher, as is presented in Figure 3. At low CO\textsubscript{2} partial pressures, carbonaceous material contains only preadsorbed CH\textsubscript{4} because the activities of adsorbed CO\textsubscript{2} molecules in the bulk mixture are very small. Further injecting of CO\textsubscript{2} molecules into the bulk mixture (i.e., an increasing of CO\textsubscript{2} partial pressure) causes an enhancement of CH\textsubscript{4} content in both studied carbonaceous materials. (See Figure 3 and the middle panel in Figure 4.) Surprisingly, some additional CH\textsubscript{4} molecules are pumped from the bulk mixture into carbonaceous micropores. It seems reasonable that adsorbed CO\textsubscript{2} molecules can be treated as a part of the external field that overall enhances the solid−fluid interactions with bulk CH\textsubscript{4} molecules. However, note that enhancement of CH\textsubscript{4} adsorption is slightly higher on the P carbon minimal surface compared with the G one. This result can be easily explained by the fact that the P carbon sample contains wider carbon micropores (see pore size distributions displayed in Figure 5). In wider micropores, the equilibrium CO\textsubscript{2}/CH\textsubscript{4} selectivity at zero coverage is reduced. We will discuss this point in detail later for simpler slit-shaped pore geometry. Further injecting of CO\textsubscript{2} molecules into the bulk mixture results in gradual displacement of CH\textsubscript{4} from carbonaceous micropores. (See the bottom panel in Figure 4.) That is why for both studied porous materials we observe clear maxima in Figure 3 (see upper and middle panels). As expected, at higher CO\textsubscript{2} partial pressures in the binary mixture, the stronger affinity of CO\textsubscript{2} to curved graphitic minimal surfaces as well as CO\textsubscript{2}−CO\textsubscript{2} interactions causes the displacement of CH\textsubscript{4} molecules from studied materials (i.e.,

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Upper panel: CO\textsubscript{2} partial pressure variation of CH\textsubscript{4} pore density in Schwarz’s Primitive (left panel) and Schoen’s Gyroid (right panel) carbon minimal surfaces. Middle panel presents composition of the binary CO\textsubscript{2}−CH\textsubscript{4} mixture in both carbonaceous materials. Bottom panel displays CH\textsubscript{4} pore density variation of the total potential energy of confined mixture. For all panels, studied partial pressures of CH\textsubscript{4} are displayed in the right middle panel.}
\end{figure}
CO2-induced cleaning of the adsorbed phase from CH4 mixture component). Moreover, we observe an interesting degeneracy phenomenon, where two different values of the total potential energy of the adsorbed mixture correspond to the same content of CH4 in the adsorbed phase. To the best of our knowledge, this is the first report showing such interesting behavior of fluid mixture confined on the nanoscale. The higher potential energy state of adsorbed molecules corresponds to the pore fluid phase enriched in CH4, whereas the lower potential energy state of adsorbed molecules corresponds to the pore fluid phase enriched in CO2. The analysis of theoretical results clearly shows that CO2-induced enhancement of CH4 adsorption as well as displacement of preadsorbed CH4 depends on the carbon pore size (compare Figures 3 and 5). This observation could have important implications in enhanced coalbed methane recovery.

To study CO2-induced enhancement and displacement of CH4 from carbonaceous micropores, we replaced the model triply periodic carbon minimal surfaces by slit-shaped carbon micropores. It has been shown that coals, carbide-derived porous carbon35,36 ordinary porous carbons32 and activated carbon fibres55−58 contain slit-shaped carbon micropores of various sizes. Regardless of the different micropore geometry, we have found a very similar trend. First, at low CO2 partial pressures in the binary CO2−CH4 mixture, adsorbed CO2 molecules induced the enhancement of CH4 storage in comparison with adsorption of pure CH4 fluid (i.e., the amount of preadsorbed CH4). For higher partial pressures of CO2 in the bulk mixture, we observe a displacement of CH4 molecules from the studied slit-shaped carbon micropores (see Figure 6). As for triply periodic carbon minimal surfaces, we notice that the pore size is crucial to control the amount of CH4 in adsorbed phase. To quantify our theoretical results, we propose to describe the variation of the CH4 pore density with the CO2 partial pressure in the bulk mixture by the following resonance-type relation

$$\rho_{\text{CH}_4} = f_0 \left[ (\omega^2 - x^2)^2 + \omega^2 x^2 \right]^{-1/2}$$

where $x \equiv \ln(P)$, $P$ denotes CO2 partial pressure in the binary CO2−CH4 mixture, and $\rho_{\text{CH}_4}$ is the CH4 pore density. The parameters $f_0$, $\omega$, and $\gamma$ controls the position and height of the maximum CH4 storage. Note that for $\gamma = (2\omega)^{1/2}$ the curve is monotonic. Although eq 6 is purely empirical, it gives precise value of the CO2 partial pressure corresponding to the maximum of CH4 pore density. From practical viewpoint, this information is very important because this point defines the minimum CO2 partial pressure that has to be overcome to induce the displacement of preadsorbed and adsorbed CH4.

We computed the maximum enhancement of CH4 in the adsorbed phase from the following expression
Here $\alpha_{\text{CH}_4}$ is given in [%], $\rho_{\text{max}}$ denotes the maximum CH$_4$ pore density induced by adsorbed CO$_2$, and $\rho_{\text{min}}$ is the CH$_4$ pore density corresponding to zero partial pressure of CO$_2$ in the binary CO$_2$–CH$_4$ mixture. Obviously, $\alpha_{\text{CH}_4} = 0$ at low CO$_2$ partial pressures in the bulk mixture because CO$_2$ molecules are not adsorbed on carbonaceous materials. Figure 7 depicts the use of eqs 6 and 7 in analysis of theoretical results.

Interestingly, the CO$_2$-induced enhancement of CH$_4$ storage is significant in wider carbon micropores. For example, in slit-shaped carbon micropore of pore size 1.61 nm and CH$_4$ partial pressure of 0.026 MPa, we can store 14 times more CH$_4$ with adsorbed CO$_2$ as compared with adsorption of pure CH$_4$ fluid. (See Table 3.) At the same time, we need higher partial pressure of CO$_2$ in the binary CO$_2$–CH$_4$ mixture to induce the displacement of CH$_4$ molecules from micropores. To explain these results, we need to analyze the differences between the carbon–CO$_2$ and carbon–CH$_4$ interaction potentials for selected pore sizes. Therefore, we computed solid–fluid potential profiles for two studied slit-shaped carbon micropores (see Figure 8). For simplicity, we assumed the spherical model for both CH$_4$ and CO$_2$ with solid–fluid parameters published by Neimark et al.$^{59,60}$ Although, this is strong simplification, especially for rod-shaped CO$_2$ molecules, we believe that the fundamental physics behind studied phenomenon is correctly captured. As would be expected, in wider carbon micropore the solid–fluid potentials for CH$_4$ and CO$_2$ are very similar, as is depicted in Figure 8. Only close to the micropore walls the carbon-CO$_2$ potential is slightly deeper as compared with the carbon-CH$_4$ one. In the remaining micropore space, the solid–fluid potential profiles are indistinguishable (i.e., the adsorption at infinite dilution is not selective toward CO$_2$ or CH$_4$). In contrast, in narrower carbon ultramicropore, the differences between carbon-CO$_2$ and carbon-CH$_4$ potential profiles are enhanced and span the entire pore space, which indicates the stronger affinity of CO$_2$ to this ultramicropore (i.e., the equilibrium CO$_2$/CH$_4$ selectivity at zero coverage is enhanced). Therefore, the displacement of preadsorbed CH$_4$ from narrower ultramicropore occurs easier (i.e., at low partial pressure of CO$_2$ in the bulk mixture) as compared with wider micropore (see Figure 6). Therefore, it is evident that enhanced adsorption field in carbon ultramicropores facilitates the nonreactive displacement of CH$_4$ by coadsorbed CO$_2$. The enhancement of the equilibrium CO$_2$/CH$_4$ selectivity, given at zero coverage by the ratio of Henry’s constants,$^{50}$ $\alpha_{\text{CO}_2/\text{CH}_4} = \left( \frac{\rho_{\text{max}}}{\rho_{\text{min}}} - 1 \right) \cdot 100\%$ (7)

Here $\alpha_{\text{CH}_4}$ is given in [%], $\rho_{\text{max}}$ denotes the maximum CH$_4$ pore density induced by adsorbed CO$_2$, and $\rho_{\text{min}}$ is the CH$_4$ pore density corresponding to zero partial pressure of CO$_2$ in the binary CO$_2$–CH$_4$ mixture. Obviously, $\alpha_{\text{CH}_4} = 0$ at low CO$_2$ partial pressures in the bulk mixture because CO$_2$ molecules are not adsorbed on carbonaceous materials. Figure 7 depicts the use of eqs 6 and 7 in analysis of theoretical results.

Figure 6. Upper panel: CO$_2$ partial pressure variation of CH$_4$ pore density in two slit-shaped carbon micropores of pore width 1.31 (left panel) and 0.66 nm (right panel). Middle panel presents composition of the binary CO$_2$–CH$_4$ mixture in studied slit-shaped carbon micropores. Bottom panel displays CH$_4$ pore density variation of the total potential energy of confined mixture. For all panels, studied partial pressures of CH$_4$ are displayed in the right middle panel.
$K_{\text{CO}_2}/K_{\text{CH}_4}$ is a key to desorb efficiently the preadsorbed CH$_4$ molecules.

**Figure 7.** Maximum enhancement of CH$_4$ storage in slit-shaped carbon ultramicropore (pore width of 0.66 nm) at 293 K. CH$_4$ pore density of 1.58 mmol cm$^{-3}$ (i.e., the adsorbed amount of preadsorbed CH$_4$) corresponds to the adsorption from the pure CH$_4$ at 0.26 MPa and 293 K. Maximum CH$_4$ pore density of 3.85 mmol cm$^{-3}$ is found for the CO$_2$ partial pressure of 0.157 MPa in the bulk mixture. (See eq 6.) The maximum enhancement of CH$_4$ storage computed from eq 7 is $\sim$144%. Black line shows the fit of the proposed resonance-type relation given by eq 6 to the simulation results.

**Figure 8.** Carbon–CH$_4$ (blue dashed lines) and carbon–CO$_2$ 10$^{-3}$–3 Steele$^{48,49}$ (black solid lines) potential profiles computed for two studied slit-shaped carbon micropores. The effective slit-shaped pore width was computed from, $H = H_g - \sigma_{ss}$, where $H_g$ denotes geometrical pore size and $\sigma_{ss} = 0.34$ nm. The solid–fluid parameters were taken from previous studies (Neimark et al.$^{50,60}$).

**Table 3. Maximum CO$_2$-Induced Enhancement of CH$_4$ Storage in Selected Slit-Shaped Carbon Micropores (see eq 7) and Studied CH$_4$ Partial Pressures in the Binary CO$_2$–CH$_4$ Mixture$^a$

<table>
<thead>
<tr>
<th>slit-shaped carbon pore width, (nm)</th>
<th>CH$_4$ partial pressure, (MPa)</th>
<th>CO$_2$ partial pressure corresponding to maximum of CH$_4$ storage, $\omega$ (MPa)</th>
<th>maximum enhancement of CH$<em>4$ storage, $\alpha</em>{CH_4}$ (%)</th>
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$^a$Note that CO$_2$ partial pressure corresponding to maximum of CH$_4$ storage (see $\omega$ in eq 6) is the starting point of CH$_4$ displacement from slit-shaped carbon micropores.
enhanced electrostatic interactions of CO2 with preadsorbed H2O molecules. As pointed by Yazaydin et al., the electrostatic interactions between CO2 quadrupolar moment and the electric field gradient of the Cu-BTC MOF are increased when H2O molecules are preadsorbed. Our theoretical results showed that CO2 induces the enhancement of CH4 uptake in carbonaceous nanopores at 293 K. However, this enhancement results mainly from the dispersion van der Waals interactions between CO2 and CH4. The electrostatic interactions between CO2 and CH4 are very weak because CH4 has no permanent electric quadrupolar moment. In the second stage, the stronger affinity of CO2 to flat/curved graphitic surfaces as well as CO2−CO2 interactions cause the displacement of CH4 molecules from carbonaceous materials. Under fixed thermodynamic conditions, the distribution of pore sizes is a crucial parameter controlling the CH4 adsorbed amount. This is because in narrow carbon micropores the equilibrium CO2/CH4 separation factor is enhanced by the surface energy.

Finally, we would like to put some comment about real enhanced coalbed methane experiment. We showed that even for assumed fast equilibration the injection of CO2−enriched industrial mixtures to carbonaceous micropores with preadsorbed CH4 is a complex phenomenon. This is because to displace the preadsorbed CH4 one needs to know the thermodynamic conditions and the pore size distribution of host material. Note that coals are structurally heterogeneous porous materials. They inherently contain mixture of narrow and wider carbonaceous pores.63−66 From our results, we make the following general conclusion: the more narrow ultramicropores a host material has, the more efficient the enhanced methane recovery is. Clearly, similar results are expected when we replace CO2 with other molecule, say X. However, we argue that if X molecule has higher affinity to carbon micropores than CO2, then we expected the better efficiency of the CH4 recovery (i.e., higher amount of desorbed CH4). This is because X/CH4 separation factor is greater as compared with CO2/CH4. This interesting aspect of the current work will be considered in our future works.

IV. CONCLUSIONS

We have presented the first comprehensive study of the binary CO2−CH4 adsorption on various CH4 preadsorbed carbonaceous materials at 293 K. From our computer experiments, we proposed two-stage mechanism of CH4 displacement from carbon nanospaces by coadsorbed CO2. In the first stage, the coadsorbed CO2 molecules induced the enhancement of CH4 adsorbed amount. This is because the adsorbed CO2 molecules enhanced the overall adsorption field that drag some additional CH4 from the bulk mixture to the micropores. In the second stage, the stronger affinity of CO2 to flat/curved graphitic surfaces as well as CO2−CO2 interactions cause the displacement of CH4 molecules from carbonaceous materials. Pore size is a key factor controlling both stages. The enhanced adsorption
field in carbon ultramicropores facilitates the nonreactive displacement of CH₄ by coadsorbed CO₂. This is because in carbon ultramicropores the equilibrium CO₂/CH₄ separation factor is increased as compared with wider micropores. The real coal sample is a not-pure dry defect-free carbon skeleton. It may contain the preadsorbed water, oxygen-containing functional groups, carbon surface defects, heteroatoms, surface partial charges, mineral contaminations, and so on. How all of these factors affect the CO₂ coadsorption and coalbed CH₄ recovery is a very difficult question to answer. However, taking into account current simulation results, we speculate that all factors enhancing the CO₂/CH₄ equilibrium selectivity should increase the efficiency of coalbed CH₄ recovery. Therefore, we speculate that preadsorbed water, oxygen-containing functional groups, carbon surface defects, heteroatoms, and surface partial charges are factors that overall enhance the CO₂/CH₄ equilibrium selectivity. This is because the quadrupole moment of CO₂ induces the specific interactions with partial charges either dispersed on the carbon surface or preadsorbed water molecules. It is difficult to make prediction about the impact of the mineral contaminates (such as ash) on the CO₂/CH₄ equilibrium selectivity. First of all, mineral contaminates can reduce the volume of adsorption space and in this way decrease the adsorbed amount from a gas phase. Mineral contaminates contain mainly metal oxides. Therefore, the CO₂/CH₄ equilibrium selectivity can be enhanced by ash. However, full understanding of displacement of CH₄ by coadsorbed CO₂ from various coal samples needs further theoretical and experimental research.

**References**
