Effects of Pore Parameters and Functional Groups in Coal on CO₂/CH₄ Adsorption

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ABSTRACT: The mechanisms of CO₂/CH₄ adsorption in coal are the theoretical foundation for CO₂ sequestration in coal seams targeted for enhanced coalbed methane recovery. Herein, by changing the model (low rank coal: WMC, middle rank coal: XM and high rank coal: CZ) with plenty of side aliphatic chains and functional groups established in the literature, the influence and mechanism of pore parameters and functional groups (−CH₃, −OH, −C₂O, −C=O) on the adsorption of CO₂ and CH₄ in different rank coals are systematically studied. Using the Connolly surface algorithm to calculate the pore volume (Vₚ) and the specific surface area (Sₘₐ) of coal with different functional groups, it can be seen that the influence of the functional group change on the pore structure is related to the coal rank. Changing the various functional groups in the original coal structure to a unified functional group (−CH₃, −OH, −C₂O, or −C=O) will increase the accessible pore volume (Vₚ) and the specific surface area (Sₘₐ), except in low-rank and middle-rank coal, where the ordered arrangement of −C=O will decrease Vₚ and Sₘₐ. The adsorption capacities of different pore parameters and functional groups were calculated by Grand Canonical Monte Carlo simulation and density functional theory. On pure adsorption, the pore parameters exert greater influence than the functional groups. By comparing the adsorption energy of the original pore structure containing functional groups and that of modified pores without functional groups, the contributions of the pore structure and original functional groups on CO₂/CH₄ adsorption are 71 and 29% and 83 and 17%, respectively. Small-diameter pores and −C₂O have a strong adsorption capacity. In terms of competitive adsorption, the −C=O functional groups and pore diameters ranging from 1.0 to 2.0 nm can significantly enhance the selectivity of CO₂ over CH₄. The CH₄ and CO₂ adsorption does not occur via rigorous monolayer adsorption; multilayer adsorption can occur for CH₄ and CO₂ with pore diameters of 1.0–2.0 and 1.0–2.2 nm, respectively, thus causing micropore filling. These quantitative results establish a foundation for the development of adsorption theory for CO₂/CH₄ in coal.

1. INTRODUCTION

Coalbed methane (CBM) is a gas that accumulates via adsorptive or free state into pores in the coal matrix, and the adsorbed gas constitutes 80 to 90% of the total gas content in coals.¹,² Hydraulic fracturing using CO₂ is a primary technique with promising results for enhancing CBM recovery.²,³ Pore systems of coal contain many micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm), in which micropores occupy a large percentage and substantially influence gas adsorption.⁴,⁵,⁶,⁷

Therefore, studying the adsorption mechanisms of CO₂ and CH₄ in the micropore of coal is beneficial for understanding CO₂ sequestration with enhanced CBM recovery and for preventing mine gas disasters.

Numerous experiment studies have investigated CO₂/CH₄ adsorption of coal; the majority of these studies used CO₂/CH₄ isothermal adsorption, low-temperature nitrogen adsorption, or scanning electron microscopy experiments to measure the influence of various factors on the gas adsorption capacity. These factors include temperature, pressure, rank, pore structure, and functional groups.⁷−¹⁷ In earlier findings, MIP, LP−N₂−Ad, LP−CO₂−Ad, and Fourier-transform infrared (FT-IR) were used to study the effect of coal pore on the CO₂/CH₄ adsorption capacity.¹¹,¹² In recent years, scanning electron microscopy and high-resolution transmission electron microscopy (HRTEM) have been used to more accurately describe the effect of the coal pore on CO₂/CH₄ adsorption.¹³,¹⁴ The main conclusions of these studies were the adsorption capacity increases with increasing rank and the amount of adsorbate decreases with increased temperature and decreased pressure. Micropores possess the largest specific area and are the main controllers of gas adsorption; in addition, the

Received: June 11, 2021
Accepted: November 9, 2021
Published: November 23, 2021
micropore content is positively correlated with the adsorption capacity. High carbon contents and numerous oxygen- and nitrogen-containing functional groups result in sorbents possessing a high adsorbate capacity.15–17 The documented experimental methods used to analyze the CO2/CH4 adsorption mechanisms have only been qualitative, and the specific effects of functional groups on adsorption cannot be quantitatively analyzed experimentally but can be evaluated by simulation.

The Langmuir monolayer,24 the Brunauer–Emmett–Teller multilayer,25 the Freundlich isotherm,26 the micro pore filling theories,27 and the gas adsorption potential28 have been used to quantitatively characterize CO2/CH4 adsorption in coal in previous literature, but the different adsorption theories do not match well with gas isothermal adsorption.29 This is due to the different basic assumptions of these models; the adsorption mechanism reflected by the theories is also different, and the interaction potential of gas adsorption in coal is still unclear.

Therefore, for quantitative analyses, systematic molecular simulations are used to investigate the adsorption capacity of CO2 and CH4.18,19,24 Previous research has proposed some microscopic models to simulate adsorption, including carbon nanotube, kerogen, and macromolecular structure models. Dang et al.20 employed Grand Canonical Monte Carlo (GCMC) simulation and density functional theory (DFT) to investigate the effects of oxygen-, nitrogen-, and sulfur-containing functional groups on CO2/CH4 adsorption in brown coal and discovered that the favorability sequence for CO2 adsorption is −C2O > pyridine-N > −C≡O > −OH > thiophene-S > −COOH; in contrast, these functional groups had less influence on CH4 adsorption. Dong et al.21 demonstrated that in middle-rank coal, the CO2 and CH4 adsorption sequences are thiophene-S > C2O > −OH > pyridine-N and thiophene-S > pyridine-N > C2O > −OH, respectively. Merkel et al.22 hypothesized that because functional groups containing oxygen have preferential sorption for CO2 selectivity (SCCO2/CH4) is higher in subbituminous coal, and −COOH and −OH exhibit weak affinity for CH4 in low-rank coals, whereas −CH3 and aromatic structure in middle- and high-rank coals significantly influence CH4 adsorption. Some researchers quantitatively analyze the influence of functional groups on adsorption by changing the functional groups in the coal structure. Song et al.23 modified the functional groups of a vitrinite coal structure by simulation to analyze the CO2/CH4 adsorption mechanism and identified adsorption sequences of −OH > −COOH > original (Ori) > −C2O > −CO > −C and −OH > −CO > −C2O > Ori > −C > −COOH for CO2 and CH4, respectively.

The adsorption capacity of coal to gas is determined by pore parameters and functional groups, and the change of the functional group will cause a change of the pore structure. However, previous literature only considered the effect of pore parameters or functional groups on adsorption, and the contribution of pore parameters and functional groups to coal adsorption capacity was not discussed. Thus, previous reports present obvious contradictory conclusions. They were lacking the elucidation for the adsorption mechanism. Therefore, to establish the quantitative relationship between macroscopic CO2/CH4 adsorption capacity and microscopic structure parameters (pore parameters and functional groups), we explored the CO2/CH4 adsorption occurrence (monolayer or multilayer) and the essential factors controlling its adsorption capacity in coal.

The main work prepared a series of macromolecular models constructed in previous literature to construct pore structure and functional group structure models that has inherent microporosity. Molecular simulation methods were used to understand the contribution of pore parameters and functional groups and occurrence of CO2/CH4 adsorption in coal. Macromolecular models of low-rank coal (low rank, Coal Bed No. 11 of Wumuchang Coal Mine in Yimin Mining Area), middle-rank (XM coal, Coal Bed No. 8 of Ximin Coal Mine in Xishan Mining Area) and high-rank coal (CZ, Coal Bed No. 3 of Chengzhuan Coal Mine in Jincheng Mining Area) are altering from various functional groups to given one functional groups, then to construct pore structure models and functional group structure models. The structure of the given functional group is used to calculate the relationship of functional groups and pore parameters by the Connolly surface algorithm. The controlling effects of pore structure and functional groups of pure CO2/CH4 and competitive adsorption of the binary mixtures (CO2 + CH4) are analyzed quantitatively by GCMC. Using the interaction potential field theory, the interaction potential and density distributions between CO2/CH4 and the pore structures were simulated. According to the pore parameters and the main force of CO2/CH4 molecules, the micropore filling adsorption region is subdivided. The adsorption capacity of the pore structures and functional groups in the macromolecular models for methane and carbon dioxide was simulated using Materials Studio 2018 software.

2. SIMULATION DETAILS

2.1. Models. 2.1.1. Ori and VFG Macromolecular Models. The low-rank (WMC: C12gH14aO18N3S; Ro,max = 0.51%),30 middle-rank (XM: C13bH12aO12N2S2; Ro,max = 1.80%),31 and high-rank (CZ: C199aH14bO9N2; Ro,max = 3.20%)31 macro-molecular models were built using ACD/NMR Predictor. FT-IR spectroscopy data provided information on oxygen functional groups, HRTEM provided information on the aromatic structure, and carbon-13 nuclear magnetic resonance (13C NMR) spectra provided the two-dimensional chemical structure. The plane macromolecular models for various original structures (Oris) are shown in Figure 1.

The functional groups in the coal structures include hydroxy (−OH), carboxyl (−COOH), ether oxygen (−C2O; contain open ether and closed ether shown in Figure S1), carboxyl (−C=O), and methyl (−CH3) groups. We have excluded carboxyl (−COOH) because it does not form when the carbon content exceeds 87%.32 To obtain a more reasonable model and a better understanding of the above-listed functional groups’ roles in displacement mechanisms, various functional group structures (VFGs; low rank-CH3, low rank-CH2, low rank-C=O, and low rank-C≡O; middle rank-CH3, middle rank-CH2, middle rank-C=O, and middle rank-C≡O; high rank-CH3, high rank-CH2, high rank-C=O, and high rank-C≡O) were generated through substitutions in the substrate of various original coal structures (Oris). There are 15 molecular models in this work, and the plane macromolecular models of Oris and VFGs are shown in Figure 1. The amount of functional groups in Oris and VFGs are shown in Table S1, and Oris and VFGs have the same number of functional groups.

2.1.2. Three-Dimensional Models. All Ori and VFG models (15 molecular models: 3 Oris and 12 VFGs) were thoroughly relaxed via the following two steps. (1) Geometry optimization: In this step, the parameters during energetic
optimizations are set using the conjugate gradient method in the Materials Studio 2018 Forcite module. The energy and force of convergence criteria were set as $2.0 \times 10^{-5}$ kcal/mol and 0.001 kcal/mol/Å, respectively. The displacement convergence criterion was set as $2.0 \times 10^{-5}$ Å, with a maximum iteration of 50,000. A smart algorithm was adopted, and the Dreiding force field was used. The electrostatic and van der Waals interactions were evaluated using the atom-based method.

(2) Annealing simulation: In this step, to overcome the energy barrier, the macromolecular model was equilibrated using the Anneal Task in the Materials Studio Forcite module. The initial and intermediate temperatures were 300 and 600 K, respectively, with 10 annealing cycles in the Dreiding force field. Then, the amorphous cell module was used to obtain three-dimensional (3D) models of energetically optimized configurations. The final energetically optimized configurations for Oris and VFGs are shown, respectively, in Figure 2 and Figure S2. The cell parameters of different molecular models are shown in Table S2.

2.1.3. Pore Structure Models. Micropores are the main site of adsorption. When the spacing is less than 0.61 nm, the methane molecule cannot enter the adsorption site, so the methane molecules cannot be adsorbed. Hence, pores of different diameters (0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, and 2.4 nm) from the macromolecular models were selected to eliminate the influence of anisotropy and heterogeneity in the coal. Pores with different configurations at each diameter were selected, and the final result calculation used average values. For example, the different pore structure configurations at 1.2 nm are shown in Figure 3.

To separate the contribution of the pore structure and functional groups and quantitatively analyze the effects of different functional groups on the adsorption capacity, we simulated the adsorption energy of CO$_2$/CH$_4$ in pure pores and in different pore functional groups (P-VFGs). The pore without a functional group (None) condition excludes all functional groups shown in Figure 4c. The P-VFGs modified the original functional groups of molecular models by substituting the functional groups with $-\text{CH}_3$, $-\text{C}_2\text{O}$, $-\text{OH}$, and $-\text{C}==\text{O}$. Figure 4 shows the steps for modifying the functional groups of a 1.2 nm pore to $-\text{C}==\text{O}$. First, a 1.2 nm pore in the coal structure (Figure 4a) was chosen, and then, the functional group was replaced with $-\text{C}==\text{O}$ (Figure 4b).

2.2. Implementation of the Simulation. 2.2.1. Isothermal Adsorption of Gas. The GCMC simulation method is used herein. The GCMC calculations were conducted in the Sorption module in Materials Studio 2018 using the optimal configurations of periodic boundary cells (PBCs), as shown in Figures 2 and S2, as adsorbents and the gaseous species as adsorbates. The adsorption isotherms and the optimal adsorption configurations for the pure gas species (CO$_2$, CH$_4$) and the binary mixtures onto the structures were obtained using the adsorption isotherm and fugacity step, respectively. The maximum numbers of iterations and equilibration steps were set as 50,000 and 10,000, respectively. The convergence criteria for energy and the fugacity step were $5 \times 10^{-4}$ kcal/mol and 20, respectively. The Ewald sum method was used for electrostatic action with a precision of $1.03 \times 10^{-3}$ kJ/mol. The Van der Waals force was calculated via the atom-based method with cubic spline truncation. The cut-off distances for electrostatic action and the Van der Waals force were both set as 12.5 Å. To ensure balance in the system, 2 $\times 10^7$ GCMC steps were adopted. The first $10^7$ steps were used to reach the balanced state, and the second $10^7$ steps were used to calculate the system adsorption isotherms and thermodynamic factors. The force field we used was COMPASS.
The ideal adsorbed solution (IAS) theory was used to predict binary adsorption isotherms from the adsorption isotherms of the pure components.\textsuperscript{36} For the binary adsorption of A and B, the IAS theory requires

\[ S = \left( \frac{x_i}{y_i} \right) \left( \frac{x_j}{y_j} \right) \]

where \( x \) and \( y \) denote the molar fraction of small molecules in the adsorbed phase and the molar fraction of small molecules in the gas phase, respectively.

\textbf{2.2.2. DFT Simulation.} The adsorption energy and low-energy structures are calculated using the DFT-D3 correction method.\textsuperscript{37,38} The local density approximation of Perdew and Wang\textsuperscript{39,40} was used to describe the exchange and correlation functions. All electron double-numerical atomic orbitals augmented by d-polarization functions were chosen as the basis set with a basis file of 3.5, and the orbital cut-off quality was set at “fine”. The adsorption energy (\( \Delta E \)) is defined as follows for single adsorption systems\textsuperscript{41}

\[ \Delta E = E_{\text{adsorbent+adsorbate}} - E_{\text{adsorbent}} - E_{\text{adsorbate}} \]

where \( E_{\text{adsorbent+adsorbate}} \) is the total energy of the adsorption system, \( E_{\text{adsorbent}} \) is the molecular energy of the VFG molecule, and \( E_{\text{adsorbate}} \) is the energy of CO\(_2\) or CH\(_4\).

\textbf{2.2.3. Interaction Potential.} The potential energy of fluid–fluid interactions is calculated using the Lennard–Jones (L–J) potential\textsuperscript{42,43}

\[ \phi_{ij} = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \]

where \( r_{ij} \) is the separation distance between the two molecules i and j, \( \sigma_{ij} \) is the fluid collision diameter, and \( \varepsilon_{ij} \) is the depth of the interaction potential well. The parameter values are listed in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & \( \sigma_i \) (Å) & \( \varepsilon_i \) (K) \\
\hline
CH\(_4\) & 3.73 & 148 \\
CO\(_2\) & 3.99 & 190 \\
\hline
\end{tabular}
\caption{L–J 12–6 Parameters\textsuperscript{44}}
\end{table}
The potential energy of interaction between a fluid molecule and a carbon atom is calculated using the L−J potential and Coulomb terms as follows:

\[ U(r_{ij}) = 4\epsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + \frac{q_i q_j}{r_{ij}} \]  

where \( r_{ij} \) is the distance between two molecules i and j, \( \sigma_{ij} \) and \( \epsilon_{ij} \) are the interaction energy parameters, and \( q_i \) and \( q_j \) are the charge of the atomic species.

### 2.2.4. Local Density Distribution

The local density distribution shows, in a 3D plot, the distribution of molecules in the adsorbed layers. It is related to the median binding affinity constant \( K_0 \) (\( K_0 \approx a^{1/n} \)), and \( P \) is the equilibrium pressure; \( n \) is the heterogeneity index (\( 0 < n < 1 \)), in which 1 indicates homogeneity and 0 indicates heterogeneity.

### 2.2.5. Langmuir–Freundlich Equation

To further understand the contribution of functional groups, the adsorption isotherms were fitted using the Langmuir–Freundlich (LF) equation, which is used to indicate whether the adsorption process is homogeneous or heterogeneous.

The LF equation is given as:

\[ \theta = \frac{\theta_m P^n}{1 + a P^n} \]

where \( \theta_m \) is the amount of adsorbates, \( \theta_m \) is the total number of binding sites, \( a \) is related to the median binding affinity constant \( K_0 \) (\( K_0 \approx a^{1/n} \)), and \( n \) is the heterogeneity index (\( 0 < n < 1 \)), in which 1 indicates homogeneity and 0 indicates heterogeneity.

### 3. RESULTS AND DISCUSSION

#### 3.1. Correlation between Functional Groups and Porosity

Chemical composition is important for pore parameters. To indicate the changes in the pore structure caused by functional groups, we used the Connolly surface algorithm to calculate the molecular surface and volume of coals using the Atom Volumes and Surfaces tool in Materials Studio 2018. The parameters of vdWScaling, ConnollyRadius, and Max Solvent Radius in the Atom Volumes and Surfaces tool were set as 1.7, 1.65, and 2.0 Å, respectively. The inaccessible pore volume (\( V^S \)), the accessible pore volume (\( V^A \)), and the specific surface area (\( S^A \)) were calculated. Physical characterization of the microporous topology and morphology is provided in Table 2, and the Atom Volume Fields are shown in Figure 5.

#### 3.2. Contribution of Functional Groups to Adsorption

Functional groups can affect gas adsorption through changing pore parameters and their own polarity and acidity. The higher the micropore content, the stronger the adsorption capacity. The C atom in CH₄ is negatively charged, and CH₄ is a nonpolar and neutral molecule; in contrast, CO₂ is positively charged and has a greater quadrupole moment and acidity. Therefore, it can be inferred that CO₂ is strongly adsorbed on basic and polar groups. The basicity (\( -C=O > C=O > CH_3 > -OH \)) and polarity (\( -OH > C=O > -C=O > -CH_3 \)) of functional groups determine the adsorption strength of CO₂ and CH₄. To better explain the role of different functional groups on CO₂/CH₄ adsorption and selectivity, we used GCMC simulation to simulate the adsorption capacity in VFGs and V-Ori models.

#### 3.2.1. Pure Adsorption

Figure 7a–f shows the adsorption amounts for pure CO₂ and CH₄ at 298 K. Different functional groups have significant influences on adsorption. The change trends of CO₂ and CH₄ are consistent, but the amplitude...
increases of CO₂ are higher than those of CH₄. Increasing the oxygen-containing functional group content will increase the chemical inertia of CH₄ and increase the negative charge on the surface of coal; thus, oxygen-containing functional groups reduce the effective adsorption potential of CH₄ molecules but increase the adsorption potential of CO₂. Thus, oxygen-containing functional groups have a stronger adsorption capacity for CO₂.

The maximum adsorption amounts of CO₂ and CH₄ both follow the sequences of low-rank C₂O > low-rank OH > low-rank Ori > low-rank CH₃ > low-rank C=O; middle-rank C₂O > middle-rank OH > middle-rank Ori > middle-rank CH₃ > middle-rank C=O; high-rank C₂O > high-rank C=O > high-rank OH > high-rank CH₃ > high-rank Ori at the same pressure and temperature. The sequence of adsorption capacity is positively correlated with the micropore volume, as shown in section 3.1. Comparing adsorption with the V_f and S_A of the VFGs, low-rank and middle-rank −C₂O and −OH, with higher V_f and S_A than −Ori, correspond to greater adsorption amounts of CO₂/CH₄. In contrast, the V_f and S_A of −C=O are smaller than those of −Ori and have an inhibiting effect on adsorption. For high rank, all functional groups improved the V_f and S_A; hence, the adsorption amounts of VFGs are all greater than those of high rank-Ori. The V_f and S_A of high rank-C₂O, high rank-C=O, and high rank-OH are similar, but the adsorption capacity order is high rank-C₂O > high rank-C=O > high rank-OH, corresponding to the basicity (−C₂O > −C=O > −CH₃ > −OH) of the functional groups. This suggests that the impact on CO₂/CH₄ adsorption capacity are pore diameter > basicity > polarity. When the pore diameters are similar, the basicity sequence is followed and the effect of polarity is weak.

This result is consistent with the results of the experiment. Liu et al.,⁵³ showed that the narrow micropores can significantly and effectively increase the CO₂ adsorption capacity, while the functional groups do not matter. Hao et al.,⁵⁴ found a positive correlation between the methane-saturated adsorption capacity and the micropore volume of coals; when the microporosity parameters of two samples were similar, the CH₄ adsorption capacity was determined by the coal surface chemistry.

The fitting process was conducted in Origin 2018 software using the LangmuirEXT1 method. The LF constants obtained are listed in Table S3. To ensure the positive parameters, R² was higher than 0.95. When comparing the values of the parameters of LF sorption isotherms, the coefficients θ_m have the same order as the pure gas adsorption amounts, as shown in Figure 6. The values of θ_m for CO₂ are larger than those for CH₄, indicating that coal can provide more binding sites for CO₂. However, the order of values for n is contrary to those of pure adsorption capacity, indicating that the adsorbed CO₂ can increase coal heterogeneity.

3.2.2. Competitive Adsorption. Figure 8 depicts the variations of competitive adsorption values (SCO₂/CH₄) for low rank, middle rank, and high rank at 298 K. Values of SCO₂/CH₄ are all apparently greater than 1.0, demonstrating the effectiveness of direct replacement of preadsorbed CH₄ by injecting CO₂. The values of SCO₂/CH₄ in different coal ranks range between 1.2 and 6.3. The calculated results agree with the experimental results.⁵⁵,⁵⁶ These results show that the simulation methods used herein are reliable.

Figure 8a gives the results of selectivity (SCO₂/CH₄) on low rank. When pressure is <4 MPa, the sequence is low-rank C=O > low-rank OH > low-rank C₂O > low-rank Ori > low-rank
CH₃. When pressure is >4 MPa, the sequence is low-rank C=O > low-rank OH > low-rank Ori > low-rank C₂O > low-rank CH₃. Figure 8b gives the results of middle rank; at low pressure (<3 MPa), the sequence is middle-rank C=O > middle-rank OH > middle-rank CH₃ > middle-rank C₂O > middle-rank Ori; when the pressure >3 MPa, the sequence is middle-rank C=O > middle-rank OH > middle-rank CH₃ > middle-rank C₂O > middle-rank Ori.
Table 3. Adsorption Energy of CO$_2$ in P-VFGs (kJ)

| pore size (nm) | ori | =O | −OH | −C$_2$O | −CH$_3$ | none |
|---------------|-----|----|-----|--------|--------|------|
| 0.6           | 60.53 | 69.48 | 45.83 | 74.43 | 60.39 | 43.64 |
| 0.8           | 60.39 | 73.32 | 43.80 | 72.52 | 59.93 | 42.15 |
| 1.0           | 54.65 | 65.58 | 42.34 | 67.45 | 55.26 | 38.91 |
| 1.2           | 46.77 | 50.38 | 39.38 | 60.75 | 52.57 | 32.83 |
| 1.4           | 40.52 | 47.12 | 36.76 | 50.94 | 49.49 | 29.13 |
| 2.0           | 39.64 | 45.92 | 30.15 | 42.28 | 40.23 | 27.66 |

Table 4. Adsorption Energy of CH$_3$ in P-VFGs (kJ)

| pore size (nm) | ori | =O | −OH | −C$_2$O | −CH$_3$ | none |
|---------------|-----|----|-----|--------|--------|------|
| 0.6           | 44.76 | 33.67 | 45.17 | 41.27 | 45.51 | 32.37 |
| 0.8           | 46.25 | 38.24 | 49.29 | 44.77 | 48.12 | 33.42 |
| 1.0           | 41.49 | 33.32 | 43.87 | 38.69 | 40.08 | 37.61 |
| 1.2           | 38.54 | 31.90 | 39.75 | 34.89 | 35.45 | 31.41 |
| 1.4           | 23.23 | 18.30 | 23.88 | 19.78 | 19.61 | 28.71 |
| 2.0           | 20.56 | 13.84 | 17.23 | 16.12 | 18.20 | 13.15 |

Table 5. Adsorption Energy of CO$_2$ in P-VFGs (kJ/mol)

| pore size (nm) | ori | =O | −OH | −C$_2$O | −CH$_3$ | none |
|---------------|-----|----|-----|--------|--------|------|
| 0.6           | 38.94 | 50.51 | 45.83 | 52.26 | 39.58 | 30.46 |
| 0.8           | 39.81 | 46.75 | 43.80 | 47.04 | 40.12 | 32.98 |
| 1.0           | 37.32 | 40.11 | 42.34 | 41.92 | 38.03 | 31.32 |
| 1.2           | 33.13 | 38.84 | 39.38 | 35.34 | 34.37 | 28.64 |
| 1.4           | 31.53 | 34.72 | 36.76 | 33.61 | 32.32 | 22.56 |
| 2.0           | 31.02 | 34.19 | 30.15 | 33.36 | 32.87 | 22.45 |

Table 6. Adsorption Energy of CH$_3$ in P-VFGs (kJ/mol)

| pore size (nm) | ori | =O | −OH | −C$_2$O | −CH$_3$ | none |
|---------------|-----|----|-----|--------|--------|------|
| 0.6           | 22.25 | 20.57 | 24.72 | 21.53 | 24.54 | 16.22 |
| 0.8           | 23.68 | 19.24 | 24.99 | 20.84 | 28.65 | 19.31 |
| 1.0           | 19.97 | 18.48 | 24.34 | 18.62 | 23.84 | 16.12 |
| 1.2           | 17.12 | 16.35 | 22.13 | 17.58 | 21.73 | 13.25 |
| 1.4           | 16.31 | 13.81 | 19.32 | 14.71 | 19.11 | 11.98 |
| 2.0           | 16.08 | 13.33 | 19.46 | 14.23 | 19.09 | 11.21 |

C=O > middle-rank CH$_3$ > middle-rank C$_2$O > middle-rank OH > middle-rank Ori. Figure 8c gives the results of the high rank; the sequence is high-rank C=O > high-rank OH > high-rank C$_2$O > high-rank CH$_3$ > high-rank Ori, and pressure has no effect on the order.

The principle of competitive adsorption is that CO$_2$ occupies the adsorption position of CH$_3$. The greater the difference in the total number of binding sites ($\theta_m$) for CO$_2$ and CH$_3$, the stronger the competitive adsorption of CO$_2$. The −C=O groups have a greater difference of $\theta_m$ as calculated in Section 3.2.1 and listed in Table S1; therefore, the VFGs with −C=O have the largest values of $S$(CO$_2$/CH$_3$).

Overall, the competitive adsorption capacity is influenced by rank, pressure, binding site ($\theta_m$) values, and pore diameter. Thus, conclusions about influencing factors for competitive adsorption are inconsistent. Du et al. stated that S$_{CO_2/CH_4}$ increased with increasing coal rank, and high-rank coal is conducive to the adsorption of CO$_2$. This opinion is identical to that of Yu et al. and Liu et al. found that the sequence of S$_{CO_2/CH_4}$ is anthracite > bituminous > lignite. However, Merkel et al. discovered that in the process of transforming subbituminous coal to anthracite, S$_{CO_2/CH_4}$ declines. Therefore, the effects of pore diameter and functional groups on the competitive adsorption of CO$_2$ and CH$_3$ need to be further investigated.

3.3. Effects of Pore Structure and Functional Groups on Adsorption Energy and Adsorption Heat.

3.3.1. Adsorption Energy. The $\Delta E$ of CO$_2$/CH$_4$ for the pure pore and P-VFGs was calculated using the DFT-D3 method using eq 5. For DFT calculations, the systems are studied by pores with different functional groups. The diameters of P-VFGs were divided into six categories: 0.6, 0.8, 1.0, 1.2, 1.4, and 2.0 nm. Figure 1 shows the pore diameter of 1.2 nm with different functional groups. In order to calculate the contributions of the pore structure and the functional groups of CO$_2$/CH$_4$, only one CO$_2$/CH$_4$ molecule in DFT calculation systems was used. The $\Delta E$s of CO$_2$ and CH$_3$ with pores without functional groups (None) and P-VFGs are shown in Tables 3 and 4, respectively. For DFT calculations, the systems are studied by pores with different functional groups. Figure 1 shows the pore diameter of 1.2 nm with different functional groups. In order to calculate the contributions of the pore structure and the functional groups of CO$_2$/CH$_4$, only one CO$_2$/CH$_4$ molecule in DFT calculation systems was used.

For the same None and P-VFG models, the $\Delta E$ values for CO$_2$ (−30.15 to −74.43 kcal/mol) are higher than those for CH$_3$ (−13.84 to −49.29 kcal/mol), indicating that CO$_2$ interacts with pure pore and P-VFGs more strongly than CH$_3$. For CO$_2$, the sequence of $\Delta E$s is 0.6 > 0.8 > 1.0 > 1.2 >
For CH$_4$, the sequence of $\Delta E$s is $0.8 > 0.6 \approx 1.0 > 1.2 > 1.4 > 2.0$ nm. When the pore diameters are $>1.0$ nm, the $\Delta E$s exhibited a declining trend. These results are consistent with experimental results, which have shown that CO$_2$ tends to adsorb in 0.6 nm pores and CH$_4$ tends to adsorb in 0.8 nm pores.$^{59}$

For the same pore diameter, the sequences of functional group $\Delta E$ values for CO$_2$ and CH$_4$ are $-\text{C}_2\text{O} > -\text{C}=\text{O} > -\text{CH}_3 > -\text{Ori} > -\text{OH}$ and $-\text{Ori} > -\text{CH}_3 > -\text{Ori} > -\text{C}_2\text{O} > -\text{C}=\text{O}$, respectively. The variations of $\Delta E$ values for the same pore diameters of CO$_2$ and CH$_4$ are caused by their polarity and basicity. The electropositive C atoms of CO$_2$ have a strong electrostatic attraction for the O atoms in the functional groups, and CO$_2$ is an acidic molecule that can react with basic groups. In contrast, the C atom in CH$_4$ is electronegative and CH$_4$ is a neutral molecule, weakening its interactions with the P-VFGs.

Compared with the $\Delta E$s of None and $-\text{Ori}$ pores, note that the functional groups enhance the adsorption energy, which is attributed to the functional groups providing a stronger electrostatic interaction of the carbon surface with CO$_2$/CH$_4$ molecules. For instance, the CO$_2$ $\Delta E$ of a pure pore is $-43.64$ kJ at 0.8 nm; however, the $\Delta E$ of $-\text{Ori}$ is $-60.39$ kJ. By comparing the adsorption energy of the Ori-containing functional groups and modified pores None, we can roughly estimate that the contributions of the pore structure and the functional groups of CO$_2$ are 71 and 29%, respectively. Similarly, the contributions of the pore structure and the functional groups of CH$_4$ are 83 and 17%, respectively. The effect of functional groups on CO$_2$ was greater than that on CH$_4$.

In recent years, many researchers have used physical and chemical methods to treat porous materials to change their functional groups. Ma et al.$^{60}$ researched that the CO$_2$ capture may depend on the functional groups in porous carbon materials, and the adsorption amount of CO$_2$ is relative to the oxygen content. Fu et al.$^{61}$ found that reducing the total amount of primary oxygenic groups including C=O, C=O, and $-\text{COOH}$ decreased the maximum CH$_4$ adsorption capability on all coals by 2.50–18.18%. These studies show that the adsorption capacity of CO$_2$/CH$_4$ is relative to the enhanced oxygen functional groups. It is basically consistent with our conclusions.

### 3.3.2. Adsorption Heat

Table 5 and Table 6 show the adsorption heat of CO$_2$/CH$_4$. The variation characteristics of adsorption heat are similar to that of adsorption energy. The

![Figure 9](https://pubs.acs.org/10.1021/acsomega.1c02573.pdf)
adsorption heat of the same amount conforms to CO$_2$>CH$_4$. The adsorption heat of CH$_4$ is much less than 42 kJ/mol which belongs to physical adsorption. The adsorption heat of CO$_2$ in 0.6/0.8 nm size with $-\equiv$O/$-\equiv$C$_2$O is higher than 42 kJ/mol. It shows that there may be chemical adsorption between CO$_2$ and coal. So, the adsorption energy of 0.6/0.8 nm size with $-\equiv$O/$-\equiv$C$_2$O is greater.

3.4. Potential Field Distribution. To further quantitatively analyze the effect of pore diameter on adsorption and the number of adsorption layers on adsorption, the pore models of various diameters built in Section 2.1.3 were used to simulate the density of CO$_2$/CH$_4$, interaction energy, and interaction potential distributions of coal and CO$_2$/CH$_4$.

Figure 9 shows the interaction energy between pores and CO$_2$/CH$_4$. The interaction energy increases first and then decreases, with increasing pore diameter. When the diameter is greater than 1.2 nm and less than 2.0 nm, the interaction potential field of CH$_4$ shows obvious intersection with each other, which means that pores in this range may generate multilayer adsorption. The intersection diameters for CO$_2$ range from 1.2 to 2.2 nm. Additionally, multilayer adsorption is caused by the van der Waals attraction exerted by the first layer of high-density gas. Multilayer adsorption is the foundation of micropore filling.  

Figure 10. Comparison of interaction potential distribution curves and density profiles for (a) CH$_4$ and (b) CO$_2$.
density profile indicates that CO$_2$/CH$_4$ may form an adsorption layer. Based on these findings, the interaction potential distribution curves and the density profiles of CO$_2$/CH$_4$ in the micropore structures were compared, as shown in Figure 10. With increasing pore diameters, the depth of the potential well and the main density peak both decrease, implying that the interaction of the wall with CO$_2$/CH$_4$ decreases and confirming that CO$_2$/CH$_4$ is mainly adsorbed in pores with diameters <2 nm. Furthermore, two peaks emerged in the density profile. The primary peak indicates the first absorbed layer close to the pore wall; after the first layer of gas is adsorbed and equilibrated, a significant secondary peak appeared. Both the density peaks correspond well to the main peak of the interaction potential. Thus, when the diameter of micropores is 1.0–2.0 nm for CH$_4$ and 1.0–2.2 nm for CO$_2$, multilayer adsorption (micropore filling) occurs.

Many researchers used a slit shape pore without functional groups to study the microscopic mechanism of gases adsorption. Li et al. found that as the breadth of the slit increased, the amount of adsorption decreased. Liu and Hou found that the density in the center of 1 nm pore is generally higher than that of the 3 nm pore. Multilayer adsorption comes into being in the 1 nm pore by CO$_2$/CH$_4$ molecules. Long et al. found that the tight adsorption amounts and adsorption heats decreased with increasing pore size. This is similar to our results, and the adsorption capacity decreases with the increase of pore size.

The selectivity of CO$_2$ over CH$_4$ indicates that CO$_2$ forms multiple layers more easily than CH$_4$ because the adsorption energy of CH$_4$ is weaker. Thus, the higher the distribution of 0.8–2.0 nm pores, the more favorable the competitive adsorption of CO$_2$. Competitive adsorption is not only affected by the micropore volume but also affected by the micropore size distribution. Li et al. discovered that the higher the proportion of the micropore (>1 nm), the higher the SCO$_2$/CH$_4$ values by experiment.

4. CONCLUSIONS

Herein, we combined the GCMC simulation, DFT, and interaction potential field to study the CO$_2$/CH$_4$ adsorption in coal pores and functional groups. The conclusions are as follows.

(1) Correlations between functional groups and pore parameters are affected by the coal rank. The consistent and ordered arrangement of −CH$_3$, −OH, −C$_3$O, and −C═O will increase the accessible pore volume (V$^\theta$) and the specific surface area (S$^\theta$), except in low-rank and middle-rank coals, where the ordered arrangement of −C═O will decrease V$^\theta$ and S$^\theta$.

(2) For pure adsorption, pore parameters exert greater influence on the adsorption of CO$_2$ and CH$_4$ than functional groups. By comparing the adsorption energy of the original pore structure containing functional groups and the modified pores without functional groups, the contributions of the pore structure and original functional groups are 71 and 29% and 83 and 17%, respectively, for CO$_2$/CH$_4$ adsorption. The greater the micropore volume, the stronger the adsorption capacity, and with increasing pore diameters, the adsorption capacity decreases.

(3) For competitive adsorption, the −C═O functional groups and pore diameters ranging from 1.2 to 2.0 nm significantly enhance the selectivity of CO$_2$ over CH$_4$. Competitive adsorption is not only affected by the micropore volume but also by the micropore size distribution.

(4) Monolayer adsorption is the main occurrence form of methane and carbon dioxide. Multilayer adsorption can occur for CH$_4$ at diameters of 1.2–2.0 nm and for CO$_2$ at diameters of 1.2–2.2 nm through the intersection of interaction energy. Multilayer adsorption is the foundation of micropore filling. The higher the distribution of 0.8–2.0 nm pores, the more favorable the competitive adsorption of CO$_2$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02573.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02573

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Author Contributions

Statement was equally contributed by all authors

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Author K.D. received funding from the National Natural Science Foundation of China (42103047). Authors Zhaizhi Wei and A.G. received funding from the Shanxi Jinzhong Science and Technology Key Research and Development Plan (Y201026).

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