

Molecular Simulation Study Based on Adsorption of Gas (CO₂, O₂, CH₄) on Coal

Lina Qu *, Zhenzhen Wang and Long Liu

School of Energy and Environment, Zhongyuan University of Technology, Zhengzhou 450007, China; wzz1834849@163.com (Z.W.)

* Correspondence: qln-66@163.com; Tel.: +86-0371-62506050

Abstract: This study aimed to further explore the adsorption properties of different gases (CO₂, O₂, and CH₄) on the coking coal surface by establishing a molecular model. Changes in the absolute adsorption capacity and the isosteric heat of adsorption of gases under different temperatures, pressures, and compositions were simulated using grand canonical Monte Carlo (GCMC) and molecular dynamics simulations. Interaction energy and energy distribution were used to analyze the adsorption behavior of gases, and the diffusion properties were investigated using the diffusion coefficient and diffusion activation energy. The absolute adsorption results fit well with the Langmuir-Freundlich model. The absolute adsorption capacity had a significant positive correlation with pressure and the corresponding mole fraction, and a significant negative correlation with temperature. The competitiveness, based on binary adsorption selectivity, was in the order of CO₂ > O₂ > CH₄. The isosteric heat of adsorption of CH₄ was slightly higher than that of O₂, and that of CO₂ was 1.49–1.64 times that of O₂ and CH₄. The isosteric heat of the adsorption of gases was also barely influenced by temperature and pressure. The interaction energy between CO₂ and coal was greater than that of O₂ or CH₄, but the high pressure and high content were not conducive to the adsorption of O₂ by CO₂. The preferred adsorption site for CO₂ was stronger than that for O₂ and CH₄, and its peak value negatively correlated with the molar fraction. The diffusion coefficient for single component gases initially increased and then decreased with increased pressure, showing a positive correlation with temperature. A close inverse correlation existed between diffusion activation energy and pressure. These results revealed the microscopic adsorption and diffusion regularities of CO₂, O₂, and CH₄ in the coal model, indicating great significance in accurately predicting coal fires.



Citation: Qu, L.; Wang, Z.; Liu, L. Molecular Simulation Study Based on Adsorption of Gas (CO₂, O₂, CH₄) on Coal. *Fire* **2023**, *6*, 355. <https://doi.org/10.3390/fire6090355>

Academic Editor: Ali Cemal Benim

Received: 18 August 2023

Revised: 31 August 2023

Accepted: 1 September 2023

Published: 11 September 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: coal spontaneous combustion; competitive adsorption; molecular simulation

1. Introduction

Under the influence of the national characteristics of “poor oil, less gas, and rich coal”, coal dominates the energy system in China [1]. However, the complex geohydrological structure of mines and other disaster-inducing factors have conferred 56% of recoverable coal seams with self-combustion tendency [2], of which about 49% are affected by combined disasters [3]. Thus, preventing and controlling coal’s spontaneous combustion has become a research hotspot in coal mine safety [4].

The initiation of coal autoignition is an extremely intricate process of coal–oxygen physicochemical adsorption. The coal first physically adsorbs oxygen to saturation, at which point the functional groups on the coal surface chemically react with the oxygen to change the molecular structure and release heat. Heat build-up leads to an increase in temperature, triggering coal’s spontaneous combustion [5]. Coal–oxygen adsorption provides the early basis for coal self-ignition, a process of significant importance in revealing the theory of coal spontaneous combustion. However, the influence of CH₄ and CO₂ in the coal seam on coal–oxygen adsorption cannot be ignored. To this end, scholars have used molecular simulations to investigate the competitive adsorption regularity for CO₂ and CH₄

in coal. Lu et al. [6] studied the physisorption process of oxygen by functional groups in coal. Their results show that physisorption begins to change into chemisorption as the adsorption amount increases. Zhou et al. [7], Yang et al. [8], Zhang et al. [9], and Ren et al. [10] used a coal macromolecular model to adsorb CH₄ and CO₂ and found that the adsorption capacity of CO₂ was stronger than that of CH₄ [11]. Yu et al. [12], Liu X et al. [13], and Dang et al. [14] investigated the impact of oxygenic groups on the competitive adsorption of CO₂, CH₄, and N₂ in coal using GCMC and density functional theory (DFT) simulations. They found that the strong quadrupole moment and polarization capacity of CO₂ makes it more selectively adsorbed by functional groups than CH₄ and N₂. Cheng et al. [15], Xiang et al. [16], and Ding et al. [17] revealed the different adsorption and diffusion mechanisms of CH₄, CO₂, and N₂ gases from three aspects: adsorption isotherms, adsorption heat, and diffusion coefficients using molecular simulation and quantum chemistry methods. They showed that the order of adsorption capacity for the three gases is CO₂ > CH₄ > N₂, whereas the diffusion capacity follows the opposite sequence. Yu et al. [18] and Tang et al. [19] conducted experimental studies on the competitive adsorption of mixed gases under different volume fractions. They found that the adsorption amount in multicomponent gases was affected by the adsorption power, molecular properties, and the partial pressure. Wang et al. [20] and Zhang et al. [21] studied the adsorption of CH₄, CO₂, N₂, O₂, and their mixed gases on a coal surface model. The presence of CO₂ was found to greatly reduce the adsorption amount of CH₄ in the binary system, and the adsorption of oxygen was more likely to be affected by the volume fraction of methane.

In summarizing the competitive adsorption among multicomponent gases in coal, previous studies have primarily focused on improving the efficiency of CBM extraction, and most of them made comparisons with N₂. Only a few studies have investigated the influence of the competitive adsorption behaviors of CH₄, CO₂, and O₂ on coal's spontaneous combustion. However, O₂ is an essential gas for the spontaneous combustion of coal, so the study of its competitive relationship with CH₄ and CO₂ in coal is an essential prerequisite for ensuring the safe operation of coal mines and preventing the occurrence of fire accidents due to the spontaneous combustion of coal. Therefore, taking CO₂, O₂, and CH₄ as the research objects, the present study used GCMC to simulate and analyze the adsorption behaviors of these gases in the molecular structure of coking coal. This research aimed to provide a theoretical basis for coal mine fire prevention at the microscopic level.

2. Construction and Simulation Method of the Coal Molecular Model

2.1. Coal Molecular Configuration

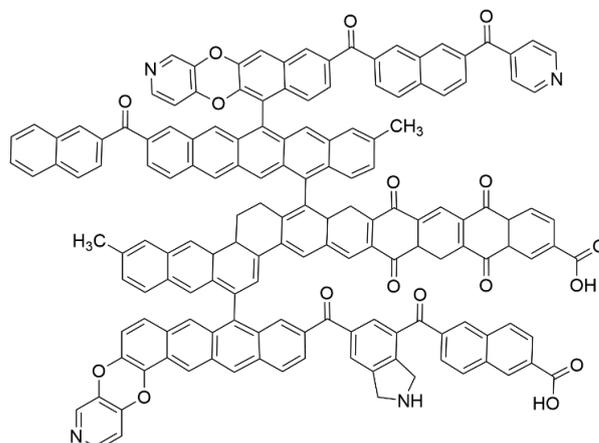
The coking coal was obtained from the 12th Coal Mine of Pingdingshan, Henan Province. For this research, elemental and industrial tests were used to analyze the coking coal, and the results are shown in Table 1. According to ¹³C-NMR, XRD, XPS, and other experiments, we obtained information on the distribution of hydrocarbon atoms, the arrangement of aromatic structures, and the presence of functional groups containing nitrogen, oxygen, and sulfur. By combining the results of the industrial analysis with the results of the elemental analysis, the molecular formula of coking coal was determined to be C₂₀₉H₁₄₀O₁₇N₄, which was derived from modeling methods described in the literature [22]. The two-dimensional structure diagram and the structural parameters are displayed in Figure 1 and Table 2, respectively.

Table 1. The basic parameters of the coal sample.

Proximate Analysis (%)				Ultimate Analysis (%)				
M _{ad}	A _{ad}	V _{daf}	FC _{ad}	C	H	O	N	S
1.68	22.64	17.3	62.58	84.02	4.70	9.33	1.88	0.07

Table 2. The structural parameters of the coking coal.

Molecular	Molecular Weight	Element Content (%)			
		C	H	O	N
$C_{209}H_{140}O_{17}N_4$	2982	84.02	4.7	9.1	1.8

**Figure 1.** The molecular configuration diagram of coal (two-dimensional).

2.2. Optimization of the Coal Macromolecule Model

Since only the structural model with the lowest energy represented the optimal configuration under study, the two-dimensional structure of coking coal was imported into Materials Studio software and the Forcite module was used to calculate MM and MD. The main purpose of MD calculation was to avoid excessive calculation of adsorption simulation due to the complex macromolecular structure. The MM parameters were [23] that the calculation method was a smart minimizer, the maximum number of iteration steps was set to 5000 steps, and the charge distribution and the force field were the charge equilibrium method and Dreiding. The electrostatic and Van der Waals values were calculated using the atom-based method. The MM calculation overcomes the disadvantage of only the local minimum value being obtained via MD. The minimum value of the whole potential energy surface was found using the annealing dynamics simulation. The MD parameters were the following [24]: the NVT ensemble (constant particle number N , volume V , and temperature T in the simulation system remain unchanged) was selected, the temperature range was 300–600 K, and it was heated up 60 K each time and cycled ten times. The temperature control program selected Nose, and the step size was 1 fs. The MM calculations were performed on the output configuration at the end of each cycle, and the parameters were set as described above. The optimized results of MM and MD are shown in Figure 2a,b, respectively. The adsorbent configuration after molecular optimization is shown in Figure 3.

Density simulation not only added periodic boundary condition to coal molecules, but also explored the optimal configuration under periodic boundary conditions. Finally, the reliability of the modeling method was verified by comparing the cell density obtained after passing the minimum energy point with the actual coal sample density. The periodic boundary conditions were added to the model using the Amorphous Cell module. The following parameters were used to simulate the density [25]: the calculation used Medium, the Dreiding was used to force field, and the charge was calculated using the charge balance method (QEq). The initial density was 0.6 g/cm^3 , the final density was 1.8 g/cm^3 , and the interval was 0.05 g/cm^3 . By analyzing the relationship between density and potential energy, it was found that the structure had the lowest potential energy when the density was 1.35 g/cm^3 . The lattice parameters of the optimal configuration are $L_x = L_y = L_z = 1.3912 \text{ nm}$, $\alpha = \beta = \gamma = 90^\circ$, as shown in Figure 2c.

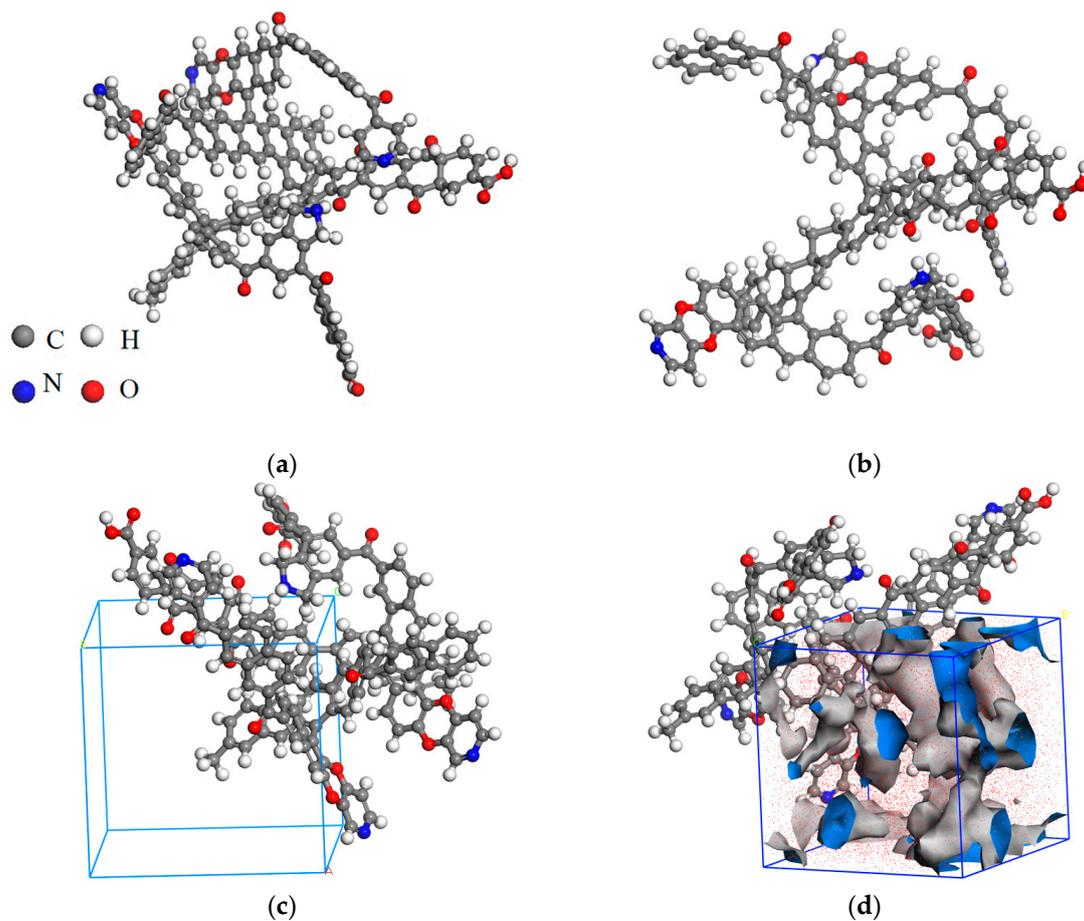


Figure 2. (a) geometry optimization, (b) annealing treatment, (c) cubic cell model, (d) connolly surface.

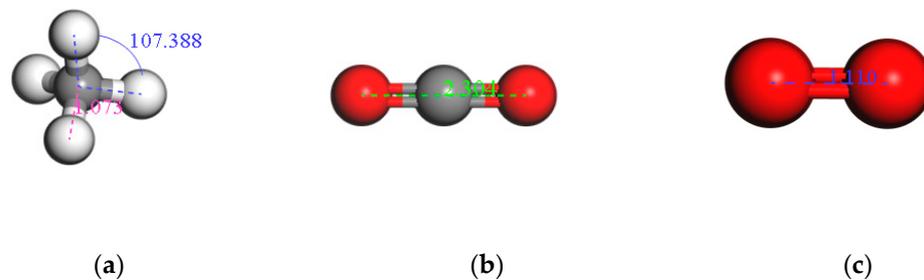


Figure 3. The optimized molecular structure of an adsorbent: (a) CH₄, (b) CO₂, and (c) O₂.

After the NPT ($P = 1$ MPa, $T = 298$ K) ensemble simulation, the final density of the model was stabilized at 1.39 g/cm³, which was close to the measured value. The effective pore volume and surface area for the model were determined using the Atom Volumes and Surfaces tool, and were 2414 m²/g and 0.0209 cm³/g. The Connolly surface of the model [26] is shown in Figure 2d.

To closely approach the real porous state of coal, a supercell molecule comprising $2 \times 2 \times 2$ original molecules of coking coal was constructed to form pores of different sizes [27]. This paper used the GCMC method to simulate the relationship between the adsorption capacity of CO₂, O₂, and CH₄ on coal surface and fugacity, wherein fugacity was converted from pressure using the Peng–Robinson equation [28]. The adsorption characteristics of gas molecules on the coal surface were investigated using the adsorption module to obtain the adsorption isotherm, adsorption site, action energy, diffusion coefficient, and adsorption selectivity. The parameters of the sorption module were set as follows [29]: the task item was Fix Pressure and the precision was Customized. The Metropolis method was used to

calculate the energy change in adsorbed gas molecules on the surface of the coal molecular model. The number of molecules N in the equilibrium state of the simulated system was obtained using the μVT ensemble (chemical potential μ , volume V , and temperature T of the model system remained unchanged). To achieve thermodynamic equilibrium and save on computation time, the total number of simulation steps was determined to be 2×10^7 Monte Carlo steps. The number of equilibrium steps was set as 1×10^7 to ensure adsorption equilibrium and the number of production steps was set as 1×10^7 to sample the exact average date. The models obtained at different temperatures and pressures using the Fix pressure method were taken as the initial model, which was optimized using MD simulation. The Dynamic task was used to calculate the kinetic coefficients, such as diffusion coefficient and diffusion activation energy.

3. Simulation Result Analysis

3.1. Absolute Adsorption Capacity

3.1.1. Single Component Gas Adsorption Capacity

The simulation data were fitted using Langmuir, Freundlich, and Langmuir–Freundlich models [30]. The Langmuir–Freundlich model could describe the entire adsorption for gases very well, and its fitting formula [31] was as follows:

$$q = \frac{abp^{1/n}}{1 + bp^{1/n}}$$

where q is the adsorption amount (mL/g), a is the gas maximum single layer adsorption amount, p is the adsorption pressure (MPa), b is the adsorption equilibrium constant (MPa^{-1}), and n is the surface heterogeneity of the adsorbent. The fitting curves of the adsorption isotherm are shown in Figure 4.

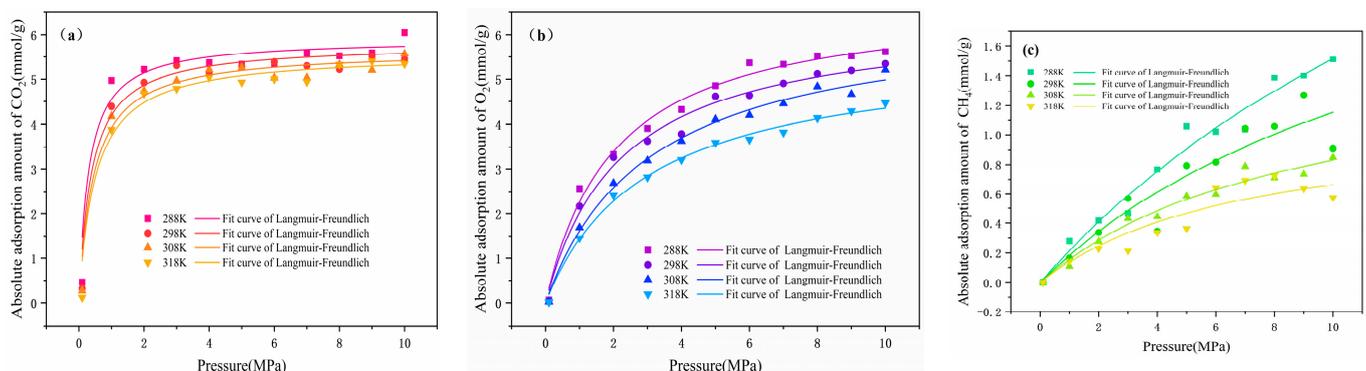


Figure 4. The adsorption isotherm and Langmuir–Freundlich fits of (a) CO_2 , (b) O_2 , and (c) CH_4 .

With increased pressure, the adsorption isotherm for CO_2 initially increased quickly and remained stable, O_2 increased slowly at the low pressure stage and then gradually became saturated, and CH_4 increased linearly. These phenomena not only showed that there was a critical value of the influence of pressure on the adsorption capacity [32], but the molecular weight of the gas also affected the adsorption amount because coal molecules had a limited effective adsorption point. Therefore, CO_2 had a high adsorption amount due to its greater molecular weight, compared to CH_4 and O_2 . In comparison with the simulation results of Qiang [33], the absolute adsorption isotherm for CO_2 in this work was found to be qualitatively in agreement, but quantitatively higher. The reason was that the hydrogen, oxygen, and nitrogen content in coking coal was higher, indicating that there were more hydroxyl, carboxyl, and methoxyl groups interacting with CO_2 . The relationship between the adsorption amount of gases under the same condition was $\text{CO}_2 > \text{O}_2 > \text{CH}_4$. The interaction energy between gases and coal molecules was an important basis for sequencing. The adsorption capacity decreased with the temperature increase. This was because the initial stage of adsorption was physisorption caused by

intermolecular suction, and the increase in temperature reduced the original weak binding force and led to desorption.

The fitting parameters and correlation coefficient of the Langmuir–Freundlich models are summarized in Table 3. All R^2 values exceeded 0.98, confirming the reliability of the Langmuir–Freundlich model. The relationship of the parameter was $a_{(CO_2)} > a_{(O_2)} > a_{(CH_4)}$, which means that CO_2 was the first gas to attain stability and had the maximum adsorption capacity. The parameter b was inversely proportional to the pressure required for saturation, indicating that the magnitude of the pressure required by the gas was $CH_4 > O_2 > CO_2$, so that the adsorption rate for CO_2 increased the fastest under a low pressure [34]. With increased temperature, the fitted parameters gradually decreased. This suggests that the temperature was not favorable to gas adsorption, but provided energy for the gas to escape from the coal surface.

Table 3. The Langmuir–Freundlich fitting parameters.

Temperature (K)	CO_2				O_2				CH_4			
	a	b	n	R^2	a	b	n	R^2	a	b	n	R^2
288	5.910	1.981	0.881	0.996	5.818	1.417	2.853	0.98	4.671	0.178	3.707	0.999
298	5.793	0.891	0.435	0.985	4.491	0.668	2.005	0.988	2.798	0.181	2.587	0.998
308	5.653	0.831	0.316	0.986	4.424	0.664	1.957	0.989	1.59	0.06	1.35	0.992
318	5.581	0.018	0.010	0.984	4.625	0.099	0.216	0.98	1.146	0.035	0.261	0.996

3.1.2. Multi-Component Gas Adsorption Capacity

To investigate the adsorption capacity between different gases, the adsorption isotherms for multi-component gases on coal at 298 K were simulated. To analyze the effect of molar fraction on adsorption behavior in the binary component system and the difference in competitive adsorption of gases in the ternary component system, the component ratios were set to 1:4, 2:3, 3:2, 4:1, and 1:1:1. The simulation results are shown in Figure 5a–d.

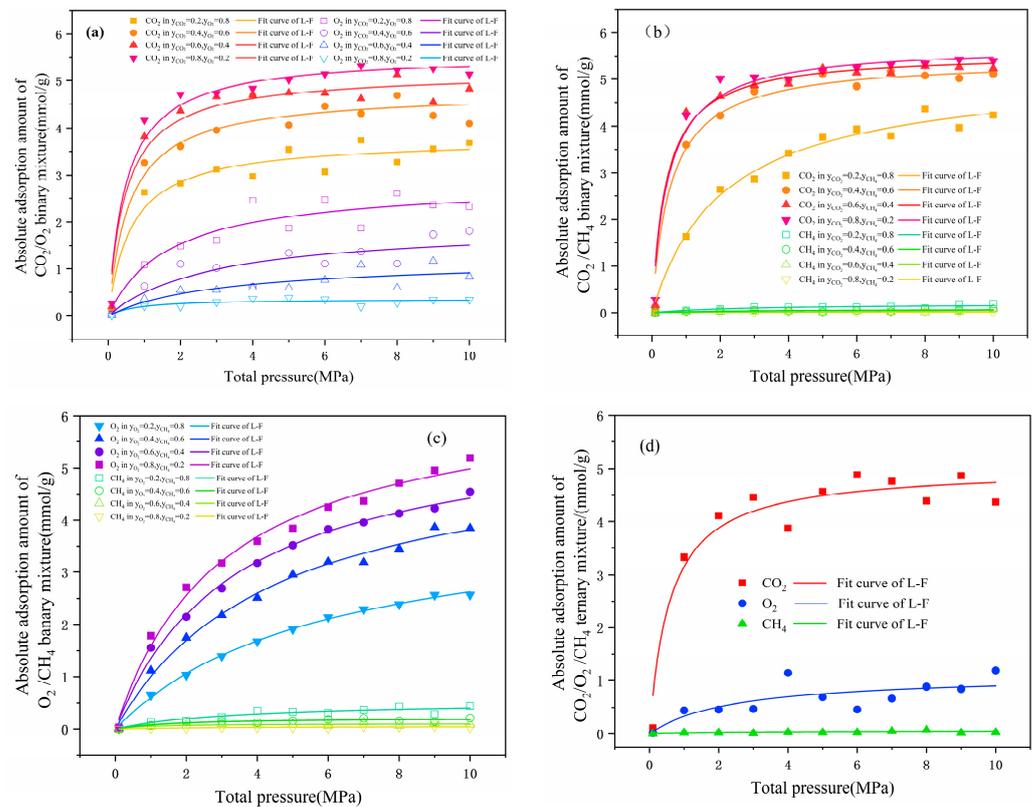


Figure 5. Absolute adsorption isotherm of binary (a–c) and ternary (d) systems.

Figure 5 shows that the adsorption amount of multi-component gas increased with increased molar fraction. In the CO₂/O₂ and CO₂/CH₄ binary system, the adsorption amounts of CO₂ were always greater than those of O₂ and CH₄ at different molar fractions, manifesting that CO₂ had a more competitive capacity than O₂ and CH₄. A comparison of Figure 5a,b revealed that the maximum values of CO₂ in the CO₂/O₂ and CO₂/CH₄ systems were 5.32 and 7.57 mmol/g, respectively, demonstrating that O₂ was more competitive than CH₄ and consistent with Figure 5c. By comparing the adsorption quantities within the pure-gas system and the CO₂/O₂/CH₄ system, it could be found that the adsorption amount for O₂ dramatically decreased. It has been shown that the presence of CO₂ affected the physical adsorption of O₂ in coal and reduced the possibility of the spontaneous combustion of coal from the source.

3.1.3. Adsorptive Selectivity

To further research the preferential adsorption ability of the gases on coal, adsorption selectivity was used to describe the competition hierarchy for multicomponent gas. $S_{m/n}$ could be defined as follows:

$$S_{m/n} = \frac{x_m/x_n}{y_m/y_n}$$

where x_m (or x_n) and y_m (or y_n) are the mole fraction of species m (or n) in the adsorbed phase and bulk phase, respectively. The adsorption selectivity was larger than 1, indicating that the competitive adsorption of adsorbate m in the multi-component was stronger than that of adsorbate n , and greater selectivity corresponded with stronger adsorption.

S_{CO_2/O_2} decreased with the increased pressure and molar fraction of CO₂, as shown in Figure 6a, indicating that high pressure and high content reduced the competitiveness of CO₂. This finding was primarily due to the CO₂ saturation being reached during the high-pressure phase, whereas O₂ was always on the rise. Figure 6b showed that S_{CO_2/CH_4} was inversely proportional to pressure and positively proportional to the molar fraction of CO₂, indicating that a higher CO₂ content corresponded with a stronger the competitive adsorption. As shown in Figure 6c, S_{O_2/CH_4} was proportional to the pressure and the molar fraction of O₂ because the amount and rate of adsorption for O₂ was far beyond that of CH₄. The analysis of adsorption selectivity revealed that the competitiveness remained at CO₂ > O₂ > CH₄, and this conclusion was confirmed by the tri-component system shown in Figure 6d.

3.2. Isotheric Heat of Adsorption

3.2.1. Single Component Gas Adsorption Heat

To some extent, the adsorption capacity could be reflected by the magnitude of the isosteric heat of adsorption. A stronger interaction energy between the gas and coal corresponded with greater isosteric heat [35]. The relationship between the adsorption heat and pressure of CO₂, O₂, and CH₄ at different temperatures is shown in Figure 7. The adsorption heat of each gas was only slightly affected by temperature and pressure. The adsorption heat of CO₂ initially decreased and then increased at around 8.625 kcal/mol. This finding may be due to the energy of the adsorbate–adsorbent interaction dominating at low pressure, whereas the adsorbate–adsorbate interaction contributed more at high pressure. Conversely, the isosteric heat for O₂ and CH₄ showed an overall decreasing trend of about 0.5–1 kcal/mol, indicating that adsorption was dominated by adsorbate–adsorbent interaction. The isosteric heat of CH₄ was a little superior to that of O₂, and that of CO₂ (8.44–8.73 kcal/mol) was about 1.49–1.56 and 1.55–1.64 times that of O₂ and CH₄, respectively. Thus, the order of adsorption heat was CO₂ > CH₄ > O₂, inconsistent with the order of the adsorption amount. This indicated that the isosteric heat of adsorption was only one of many factors affecting the adsorption capacity, which reflected the adsorption capacity to a certain extent. Because the heat levels of CO₂, O₂, and CH₄ were less than 10 kcal/mol, the adsorption on the coal surface was a physical process [36].

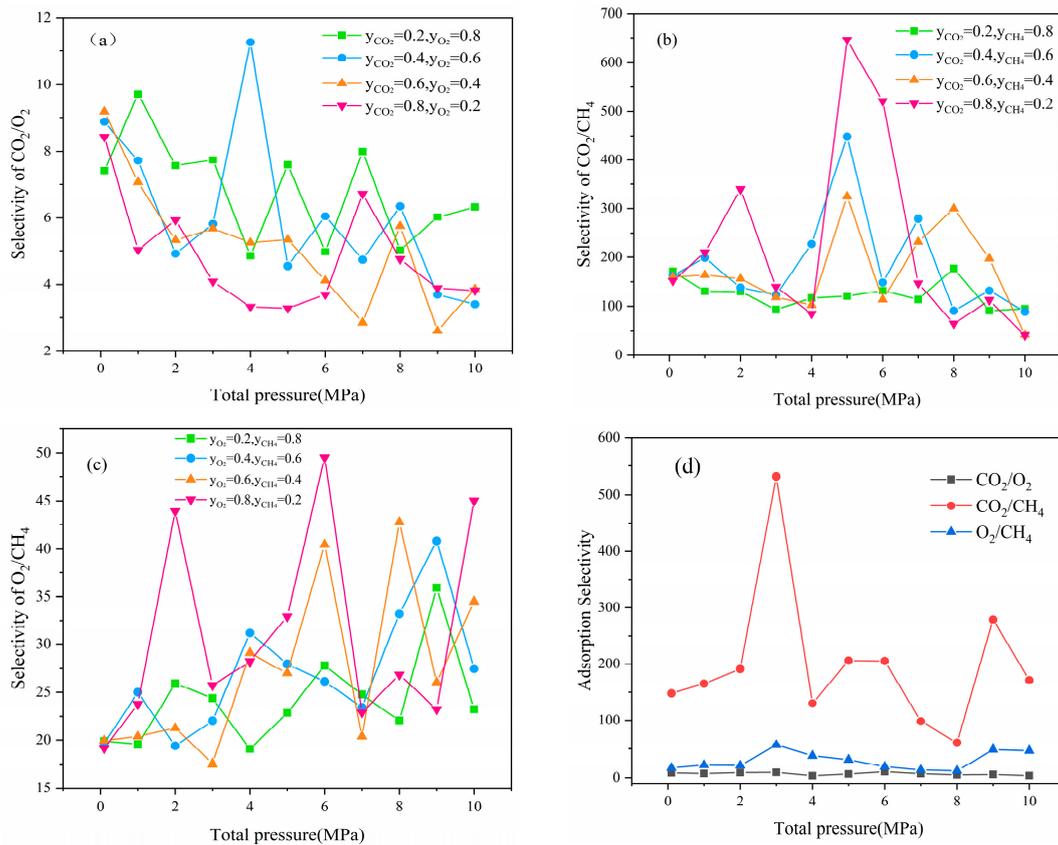


Figure 6. Adsorption selectivity of binary (a–c) and ternary (d) systems.

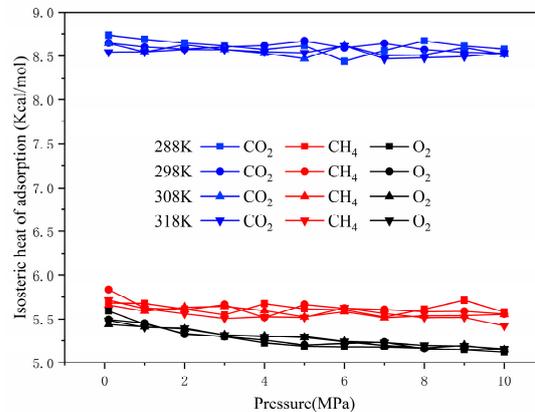


Figure 7. The isosteric adsorption heat of single component gas.

Henry’s law of adsorption describes the linear relationship between adsorption amount and equilibrium pressure at low pressure, and the formula was as follows:

$$n = K_H P$$

where n is the adsorbing capacity, K_H is the Henry constant, and P is the adsorption pressure. The Henry constant could characterize the adsorbate affinity, and it decreased with decreased K_H . The relationship of adsorption affinity for three gases was $CO_2 > O_2 > CH_4$, as shown in Figure 8. This result was due to the permanent quadrupole moment of the CO_2 molecule, which created a stronger electrostatic force on the surface of coal molecules [37]. The negative correlation showed that the affinity of these gases could be reduced by the creasing temperature. The K_H values of CO_2 were more sensitive to temperature changes, and that of CH_4 slowly decreased with increased temperature.

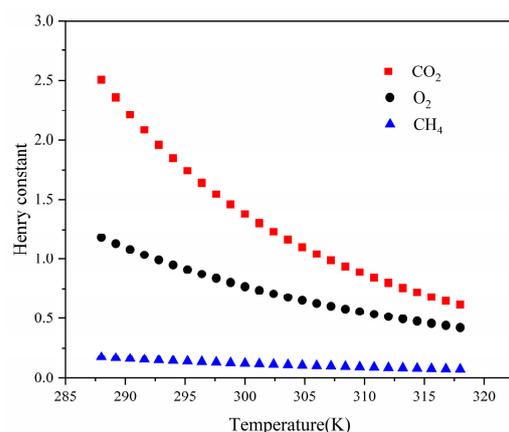


Figure 8. The Henry constant for single component gas.

3.2.2. Multi-Component Gas Adsorption Heat

The isosteric heat of adsorption in multi-component systems is shown in Figure 9, and it depended primarily on gas species and the system associated with it. Figure 9a shows that the adsorption heat for CO₂ was proportional to its molar coefficient in the CO₂/CH₄ system, but inversely proportional in the CO₂/O₂ system, consistent with the trend of adsorption selectivity in binary systems. Influenced by the competition between CO₂ and CH₄, the adsorption heat of O₂ in the CO₂/O₂ and O₂/CH₄ systems differed. The adsorption heat of O₂ decreased with increased molar fraction, which was contrary to that of CH₄, indicating that the high CH₄ content was more competitive than that of O₂. By comparison with Figure 9b and c, it could be seen that the adsorption heat of O₂ and CH₄ in the O₂/CH₄ system followed the same trend as that of pure gas, whereas it fluctuated more when CO₂ was involved. This phenomenon was due to the adsorption heat of pure CO₂, showing a local minimum that could be found only in strongly adsorbed gas [38]. The order of adsorption heat of gases in the CO₂/O₂/CH₄ system was compatible with that of pure gases. The change trends for O₂ and CH₄ showed more obvious fluctuations than those of CO₂, as shown in Figure 9d. This finding indicated a strong competition between O₂ and CH₄ for adsorption heat.

3.3. Interaction Energy

The interaction energies of CO₂, O₂, and CH₄, including van der Waals energy and electrostatic energy, were analyzed at different molar fractions in multi-component systems to further investigate the effect of competitive adsorption of gases for the interaction energy [39]. The results are shown in Figure 10.

As shown in Figure 10a,b, the van der Waals energy accounted for more than 79% and 77% of the total interaction energy in the CO₂/O₂ and CO₂/CH₄ systems, respectively, whereas the rest of the electrostatic energy originated from CO₂. This was because CO₂ was electrically charged and generated electrostatic energy when adsorbed. Meanwhile, the higher molar fraction for CO₂ corresponded with stronger interaction energy, indicating that it was more likely to adsorb than O₂ and CH₄, and the adsorption system was more stable. For the CO₂/O₂ system, the interaction energy was slightly reduced when the pressure exceeded 8 MPa and the molar fraction of CO₂ exceeded 60%, demonstrating that the high pressure and high content reduced the competitiveness of CO₂. For O₂/CH₄ binary systems, up to 98% of the total energy of interaction was van der Waals energy, and only a small amount of energy originated from electrostatic energy. The interaction energy was proportional to the pressure and the molar fraction of O₂, indicating that O₂ was more stable than CH₄. The results showed that the relationship of the adsorption stability of the gases was CO₂ > O₂ > CH₄, which was consistent with the relationship of adsorption amount.

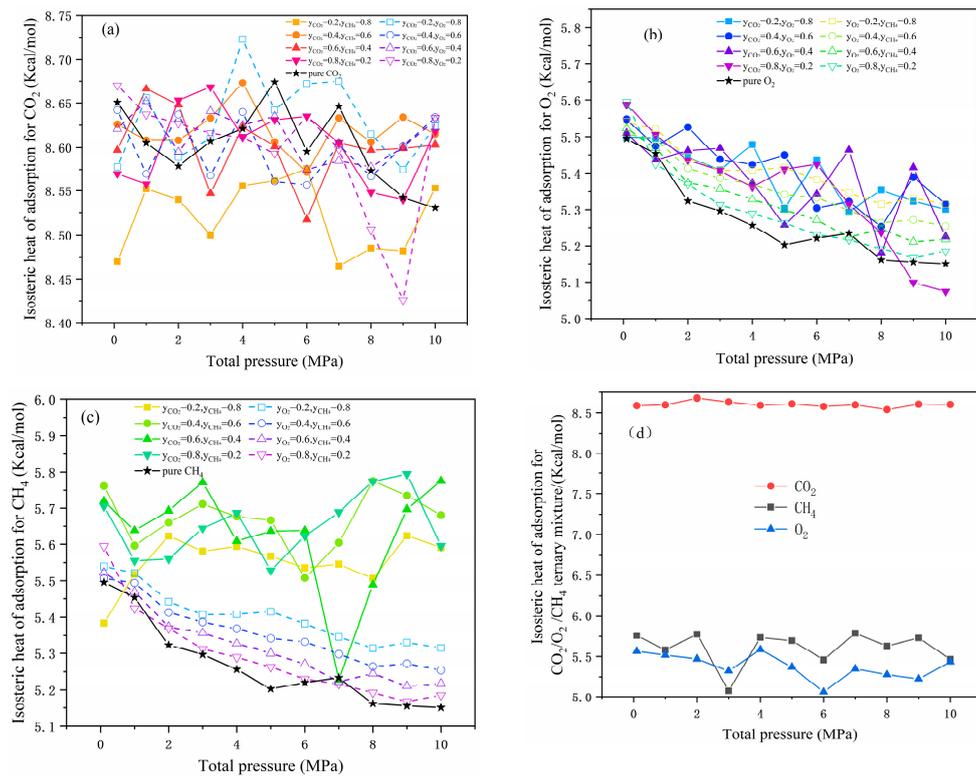


Figure 9. The isosteric heat of adsorption of CO₂, O₂, and CH₄ in binary (a–c) and ternary (d) systems.

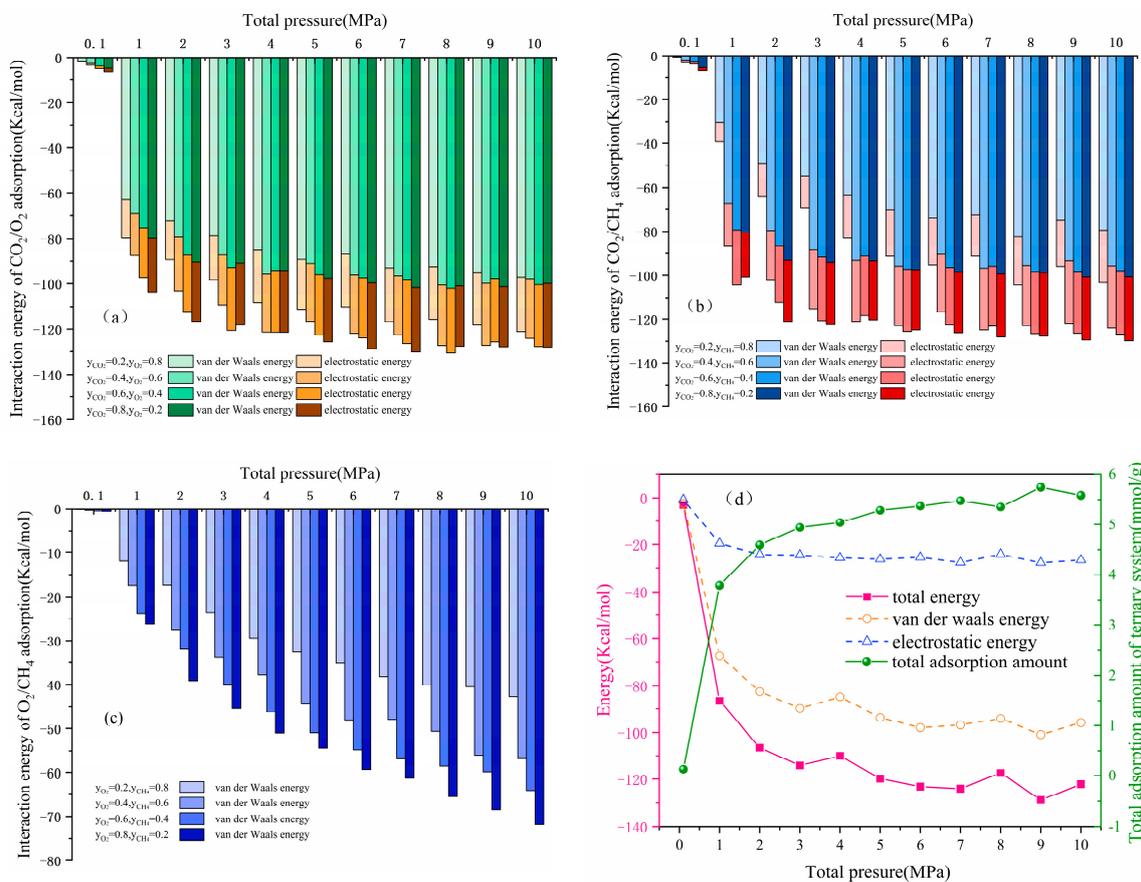


Figure 10. Interaction energy: (a) in the CO₂/O₂ system; (b) in the CO₂/CH₄ system; (c) in the O₂/CH₄ system; and (d) the total energy and adsorption amount in the CO₂/O₂/CH₄ system.

As shown in Figure 10d, the interaction energy in the CO₂/O₂/CH₄ system decreased from -2.962 kcal/mol to -122.163 kcal/mol with the pressure from 0.1 MPa to 10 MPa. The van der Waals energy accounted for more than 73%. The larger the absolute value of the interaction energy, the more prone it was to adsorb. The van der Waals energy, electrostatic energy, and total energy initially increased rapidly and then slowly with increased pressure, which was consistent with the increasing trend of adsorption capacity under the CO₂/O₂/CH₄ system [40].

3.4. Energy Distribution

The adsorbed sites could be identified using the energy distribution and be used to analyze competitive adsorption. Larger negative values indicated a stronger interaction energy and more favorable adsorption sites [41]. The energy distribution of pure CO₂, O₂, and CH₄ at different temperatures was shown in Figure 11a. The preferential adsorption site for CO₂ was lower than O₂ or CH₄, and the peak for O₂ was almost equal to that for CH₄. This was consistent with the order of equal heat of adsorption. The distinct potential energy peak was around -10.5 kcal/mol, corresponding with favorable adsorption sites for CO₂. Its peak decreased with increased temperature, which was because the temperature stimulated the activity of CO₂ molecules, so that the adsorbed gas molecules began to diffuse. Another peak at around -6.5 kcal/mol represented the favorable adsorption sites for O₂ and CH₄. The peaks of the preferential adsorption sites for O₂ and CH₄ moved toward the lower energy region with increased pressure, and a new peak at -4 kcal/mol formed at the secondary adsorption site. This finding was primarily due to the increase in adsorption volume caused by pressure, so that the priority adsorption sites gradually became saturated. Then, a large number of gas molecules shifted to the secondary adsorption sites, resulting in a movement in the relative importance of the adsorption sites.

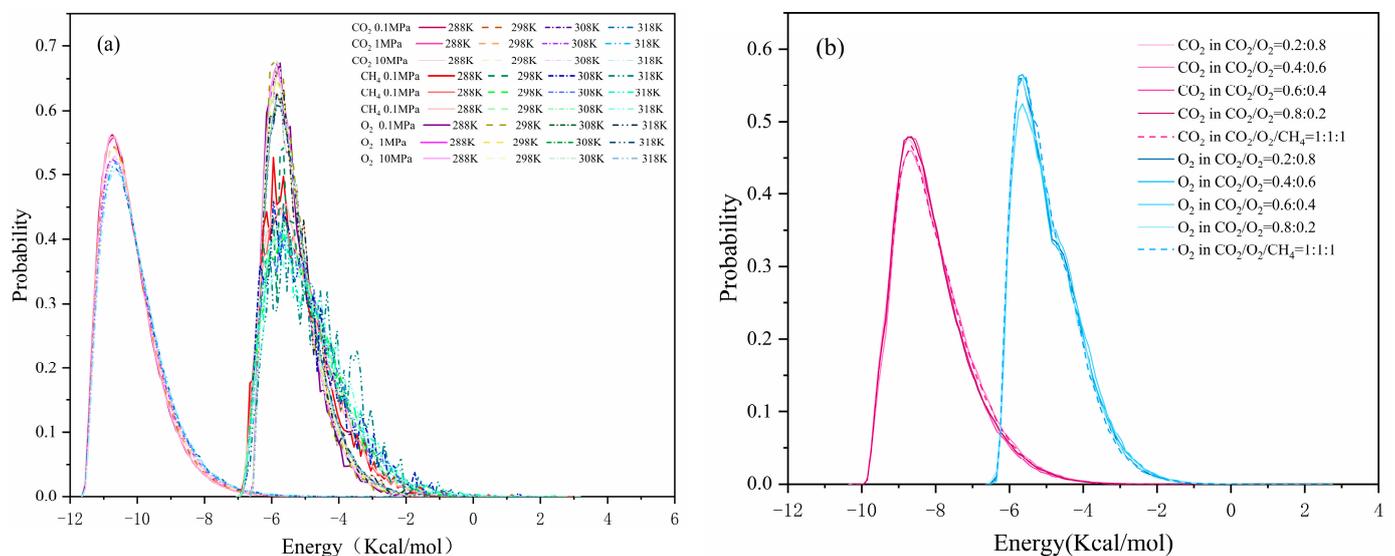


Figure 11. Cont.

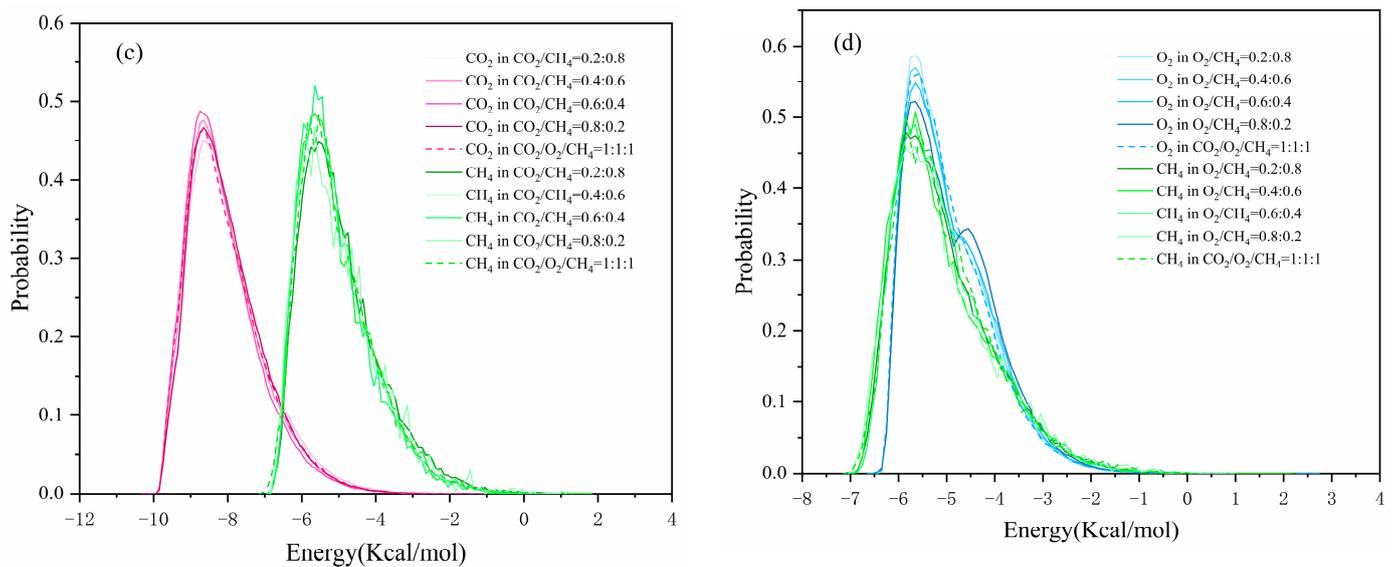


Figure 11. Energy distribution: (a,b) in a single component adsorption system; (c,d) in different adsorption systems.

The energy distribution of gases in the multi-component systems was compared at different molar fractions in order to study competition among adsorption sites, as shown in Figure 11b–d. In the CO₂/O₂ system, the peak value of the preferential adsorption site increased with increased molar fraction, implying that CO₂ and O₂ gradually reached saturation with increased adsorption capacity. The potential energy shifted to the right and the peak decreased with increased molar fraction in the CO₂/CH₄ system, showing that the high content did not facilitate the competitive adsorption of gas molecules at the preferred site. By comparing the energy–distribution curve of O₂ in the CO₂/O₂ and O₂/CH₄ systems, we found that adding CH₄ increased the peak at the second adsorption site. This finding indicated that the presence of CH₄ forced the O₂ molecules to diffuse away from the preferred adsorption site, thereby inhibiting O₂ from reaching saturation. The molecular proportion of the preferred adsorption site for O₂ (−5 kcal/mol) in the binary components was reduced.

3.5. Diffusion Property

When gas molecules made contact with the coal surface, different pressures and concentration gradients were formed by different adsorption capacities. The gas diffused from high to low under the gradient, which follows the microscopic principle of diffusion [42]. The self-diffusion coefficients of CO₂, O₂, and CH₄ were calculated using MD simulation to reveal the diffusion regularity of the gas on coal [43]. From the Einstein diffusion equation, the D_s could be calculated as follows [44]:

$$D_s = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\{ \sum_{i=1}^N [r_i(t) - r_i(0)] \right\}^2 = \frac{k_{MSD}}{6}$$

where K_{MSD} is the slope of the fitting curve of MSD , and $MSD(t) = \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle$;

N is the number of gas molecules; $r_i(t)$ is the Cartesian position vector of gas molecule in the microcrystallite at the time t ; and $r_i(0)$ is the initial position vector of the gas molecule. The diffusion coefficient and diffusion activation energy for gases on coal at different pressures are depicted in Figure 12.

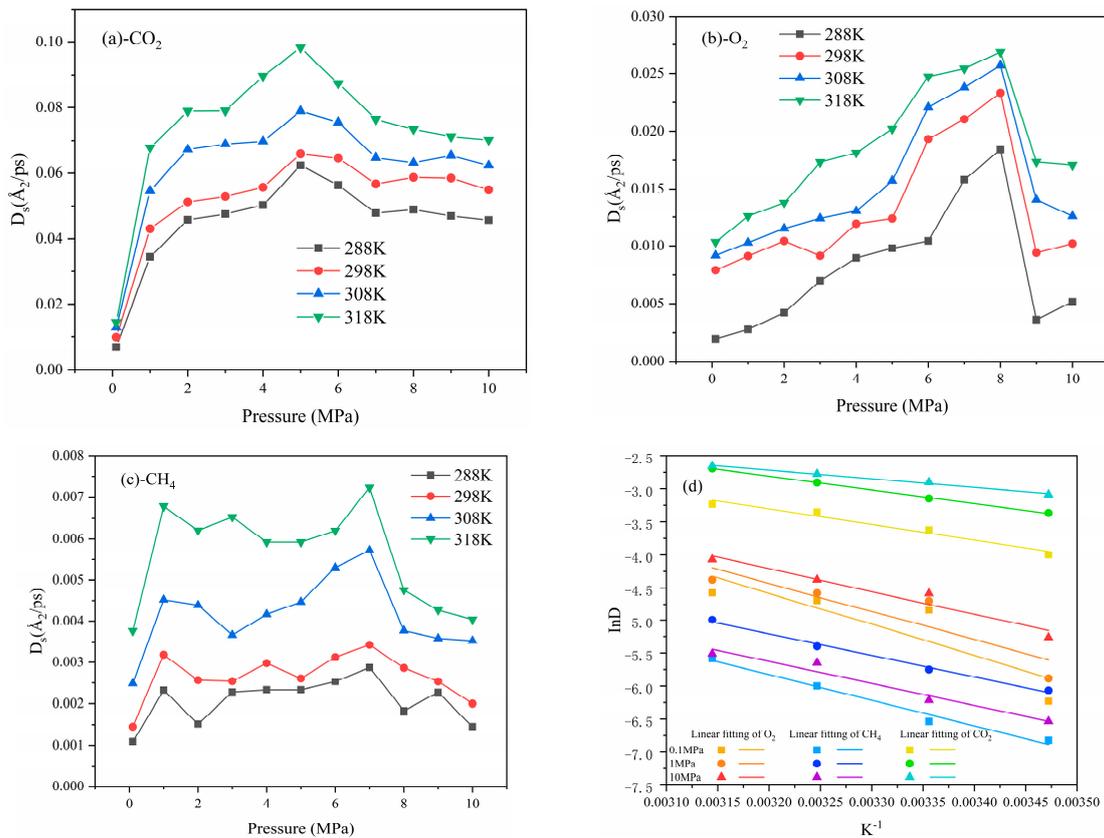


Figure 12. The self-diffusion coefficient (a–c) and the diffusion activation energy (d) of CO₂, O₂, and CH₄.

The self-diffusion coefficient of gases was positively correlated with temperature because the higher temperature corresponded with the higher internal energy of the molecules. According to the law of conserving energy, the internal energy between molecules could be converted into kinetic energy, thereby intensifying the movement of molecules and making it easier for them to diffuse. The relationship between the self-diffusion coefficients of the gas was CO₂ > O₂ > CH₄ at the same temperature, consistent with the results of Kelemen et al. [45]. The self-diffusion coefficient initially increased and then decreased with pressure. The main reason for the reduction was that gas molecules stacked up more tightly and interacted more strongly under high pressure.

The diffusion of gas in coal molecules was an activation process. The diffusion activation energy could be reckoned using the Arrhenius equation [46], and the specific formula is as follows:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right)$$

where D_0 is the pre-exponential factor; E_a is the apparent activation energy, kcal/mol; R is the ideal gas constant; and T is the temperature, K. $\ln D$ is fitted well to the reciprocal of temperature, and the calculated result is listed in Table 4. The activation energy of gas diffusion was found to be negatively correlated with pressure, and the activation energy of O₂ was approximately twice that of CO₂.

Table 4. The diffusion activation energy of CO₂, O₂, and CH₄.

Pressure	CO ₂	O ₂	CH ₄
0.1 MPa	19.65	39.60	32.29
1 MPa	17.25	35.83	27.12
10 MPa	10.83	29.05	27.73

4. Conclusions

To research the microcosm mechanism of CO₂, O₂, and CH₄ adsorption and diffusion on coal, a realistic macromolecular coal model was established. GCMC and MD molecular simulations were performed in single, binary, and ternary systems, considering the effect of temperature, pressure, and molar fraction.

(1) Adsorption isotherms were well fitted with the Langmuir–Freundlich model. The absolute adsorption amount was directly proportional to the pressure and inversely to the temperature. The adsorption of multi-component gases showed that adsorption amount was proportional to the molar fraction, but high pressure and high content reduced the competitiveness for CO₂. The competitive capacities were CO₂ > O₂ > CH₄, based on adsorption selectivity. By comparing the adsorption amount of O₂ under different component systems, we found that CO₂ significantly reduced the adsorption amount of O₂.

(2) The isosteric heat of adsorption of CO₂ (8.44–8.73 kcal/mol) was much greater than that of O₂ or CH₄ (5.12–5.83 kcal/mol). The difference in order between the adsorption quantity and the adsorption heat for the three gases meant that the adsorption amount was influenced by the adsorption heat, and many other factors. The adsorption heat was affected by the molar fraction and competition from other gases in mixed adsorption systems, which changed the adsorption sites and adsorption spaces and influenced the interaction energy. The presence of CO₂ affected the trend of the equivalent heat of adsorption of another gas with which it competed, and the existence of CH₄ caused large fluctuations in the adsorption heat of O₂.

(3) The electrostatic energy and high van der Waals energy between CO₂ and coal resulted in an interaction greater than with O₂ and CH₄. The greater interaction energy corresponded with the greater adsorption amount. In a competitive adsorption system, CO₂ and CH₄ changed the relative importance of the competitive adsorption sites for O₂, thereby inhibiting O₂ adsorption. The gas diffusion coefficient was inversely correlated with the temperature under the same pressure. The diffusion coefficient increased and then decreased with increased pressure at the same temperature. The order of diffusion activation energy was O₂ > CH₄ > CO₂, which was negatively correlated with pressure.

Author Contributions: Conceptualization, L.Q. and Z.W.; methodology, Z.W.; software, L.Q.; validation, L.Q., Z.W. and L.L.; formal analysis, Z.W.; investigation, Z.W.; resources, L.Q.; data curation, Z.W.; writing—original draft preparation, Z.W.; writing—review and editing, Z.W.; supervision, L.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the National Science Foundation of China (51804355) and the Research and Innovation Project of Zhongyuan University of Technology (YKY2023ZK13).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data unavailable due to privacy.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wu, K. Simulation of Characteristics of Coal and Oxygen Adsorption with Quantum Chemistry Methods. Master's Thesis, Xi'an University of Science and Technology, Xi'an, China, 2011.
2. Cui, L. Present Status and Countermeasure Consideration on Comprehensive Utilization of China Coal Resources. *Coal Econ. Res.* **2013**, *33*, 46–47+66.
3. Yuan, S. Gas Management Concept and Coal and Gas Co-mining Technology. *Energy Energy Conserv.* **2018**, *10*, 151–152.
4. Xu, Y. Research on Macro Featured Parameters and Test Methods of Coal Spontaneous Combustion Character. Master's Thesis, Xi'an University of Science and Technology, Xi'an, China, 2014.
5. Chen, L.; Zhang, Y. Study on influence laws of oxygen concentration on thermal effect of coal low-temperature oxidation. *J. Saf. Sci. Technol.* **2020**, *16*, 49–54.
6. Lu, J.; He, Y.; Cheng, G. Construction of Lignite Macromolecular Model and its Analysis on Physisorption Oxygen at Low Temperatures. *Min. Res. Dev.* **2021**, *41*, 58–66.

7. Zhou, W.; Wang, H.; Zhang, Z.; Chen, H.; Liu, X. Molecular simulation of CO₂/CH₄/H₂O competitive adsorption and diffusion in brown coal. *RSC Adv.* **2019**, *9*, 3004–3011. [[CrossRef](#)]
8. Yang, S. Study on the Microstructure of Water-Bearing Tectonic Coal and Its Adsorption Characteristics of CH₄ and CO₂. Master's Thesis, Qingdao University of Technology, Qingdao, China, 2021.
9. Zhang, J.; Liu, K.; Clennell, M.; Dewhurst, D.; Pervukhina, M. Molecular simulation of CO₂–CH₄ competitive adsorption and induced coal swelling. *Fuel* **2015**, *160*, 309–317. [[CrossRef](#)]
10. Ren, Z. The Studies on Adsorption of CH₄, CO₂ Gas on the Antracite Coal of Yang Quan. Master's Thesis, Henan Polytechnic University, Jiaozuo, China, 2010.
11. Allen, M.P.; Tildesley, D.J. *Computer Simulation of Liquids*; Oxford University Press: Oxford, UK, 2017.
12. Yu, S.; Bo, J.; Fengjuan, L. Competitive adsorption of CO₂/N₂/CH₄ onto coal vitrinite macromolecular: Effects of electrostatic interactions and oxygen functionalities. *Fuel* **2019**, *235*, 23–38. [[CrossRef](#)]
13. Liu, X.-Q.; He, X.; Qiu, N.-X.; Yang, X.; Tian, Z.-Y.; Li, M.-J.; Xue, Y. Molecular simulation of CH₄, CO₂, H₂O and N₂ molecules adsorption on heterogeneous surface models of coal. *Appl. Surf. Sci.* **2016**, *389*, 894–905. [[CrossRef](#)]
14. Dang, Y.; Zhao, L.; Lu, X.; Xu, J.; Sang, P.; Guo, S.; Zhu, H.; Guo, W. Molecular simulation of CO₂/CH₄ adsorption in brown coal: Effect of oxygen-, nitrogen-, and sulfur-containing functional groups. *Appl. Surf. Sci.* **2017**, *423*, 33–42. [[CrossRef](#)]
15. Cheng, G.; Li, Y.; Zhang, M.; Cao, Y. Simulation of the adsorption behavior of CO₂/N₂/O₂ and H₂O molecules in lignite. *J. China Coal Soc.* **2021**, *46*, 960–969.
16. Xiang, J.; Zheng, F.; Liang, H. Molecular simulation of the CH₄/CO₂/H₂O adsorption onto the molecular structure of coal. *Sci. China Earth Sci.* **2014**, *44*, 1418–1428. [[CrossRef](#)]
17. Yi, D. Research on the Mechanism of CH₄, CO₂, H₂O and O₂ Adsorption on Coal Molecule. Master's Thesis, School of Energy, Power and Mechanical Engineering, Beijing, China, 2018.
18. Yu, B. *Experimental Study of Yang Quan anthracite's adsorption behavior of binary-component mixtures(N₂-CH₄)*; Henan Polytechnic University: Jiaozuo, China, 2010.
19. Tang, S.; Han, D. Adsorption and desorption of multi element gas by coal. *Coal Sci. Technol.* **2002**, *30*, 58–60.
20. Wang, S.; Hu, Y.; Yang, X.; Liu, G.; He, Y. Examination of adsorption behaviors of carbon dioxide and methane in oxidized coal seams. *Fuel* **2020**, *273*, 117599. [[CrossRef](#)]
21. Zhang, Q.; Liu, W.; Li, N.; Duan, C. Experimental Study on Adsorption Characteristics of CH₄, CO₂ and Their Multi-component Gases in Huainan C₁₃ Coal. *Saf. Coal Mines* **2019**, *50*, 14–17.
22. Qu, L.; Liu, L.; Chen, J.; Wang, Z. Molecular Model Construction and Optimization Study of Gas Coal in the Huainan Mining Area. *Processes* **2022**, *11*, 73. [[CrossRef](#)]
23. Li, Z.; Wang, Y.; Li, P.; Li, H.; Bai, H.; Guo, Q. Macromolecular model construction and quantum chemical calculation of Ningdong Hongshiwang coal. *CIESC J.* **2018**, *69*, 2208–2216.
24. Jianbo, J. Construction of Structural Model and Molecular Simulation of Methane Formation Mechanism during Coal Pyrolysis for Shendong Vitrinite. Ph.D. Dissertation, Taiyuan University of Technology, Taiyuan, China, 2010.
25. Zhu, H.; He, X.; Huo, Y.; Xie, Y.; Wang, W.; Fang, S. Construction and optimization of lignite molecular structure model. *J. Min. Sci. Technol.* **2021**, *6*, 429–437.
26. Gelb, L.D.; Gubbins, K. Pore size distributions in porous glasses: A computer simulation study. *Langmuir* **1999**, *15*, 305–308. [[CrossRef](#)]
27. Gao, D.; Hong, L.; Wang, J.; Zheng, D. Adsorption simulation of methane on coals with different metamorphic grades. *AIP Adv.* **2019**, *9*, 095108. [[CrossRef](#)]
28. Gao, D.; Hong, L.; Wang, J.; Zheng, D. Molecular simulation of gas adsorption characteristics and diffusion in micropores of lignite. *Fuel* **2020**, *269*, 117443. [[CrossRef](#)]
29. Wu, S.; Jin, Z.; Deng, C. Molecular simulation of coal-fired plant flue gas competitive adsorption and diffusion on coal. *Fuel* **2019**, *239*, 87–96. [[CrossRef](#)]
30. Zheng, Y.; Li, Q.; Yuan, C.; Tao, Q.; Zhao, Y.; Zhang, G.; Liu, J.; Qi, G. Thermodynamic analysis of high-pressure methane adsorption on coal-based activated carbon. *Fuel* **2018**, *230*, 172–184. [[CrossRef](#)]
31. Li, J.; Li, B.; Ren, C.; Zhang, Y.; Wang, B. An adsorption model for evaluating methane adsorption capacity in shale under various pressures and moisture. *J. Nat. Gas Sci. Eng.* **2020**, *81*, 103426. [[CrossRef](#)]
32. Billemont, P.; Coasne, B.; De Weireld, G. An experimental and molecular simulation study of the adsorption of carbon dioxide and methane in nanoporous carbons in the presence of water. *Langmuir* **2011**, *27*, 1015–1024. [[CrossRef](#)] [[PubMed](#)]
33. Qiang, Q. Study on Competitive Adsorption Mechanism of Pingdingshan Bituminous Coal for Gas under Different Moisture Conditions. Master's Thesis, Inner Mongolia University of Science and Technology, Baotou, China, 2022.
34. Li, S.-G.; Bai, Y.; Lin, H.-F.; Shu, C.-M.; Yan, M.; Laiwang, B. Molecular simulation of adsorption of gas in coal slit model under the action of liquid nitrogen. *Fuel* **2019**, *255*, 115775. [[CrossRef](#)]
35. Wen, H.; Tang, R.; Zhang, D.; Dai, A.; Fan, S.; Zhai, X. Molecular simulation study on adsorption and diffusion of CO in bituminous coal. *J. Saf. Sci. Technol.* **2022**, *18*, 95–101.
36. Wu, S. Molecular Simulation Research on Mechanism of Coal Spontaneous Combustion Prevention and Storage of Flue Gas. Ph.D. Dissertation, Liaoning Technical University, Jinzhou, China, 2019.

37. Wang, L.; Wang, Z.; Li, X.; Yang, Y. Molecular dynamics mechanism of CH₄ diffusion inhibition by low temperature in anthracite microcrystallites. *ACS Omega* **2020**, *5*, 23420–23428. [[CrossRef](#)]
38. Sui, H.; Yao, J. Effect of surface chemistry for CH₄/CO₂ adsorption in kerogen: A molecular simulation study. *J. Nat. Gas Sci. Eng.* **2016**, *31*, 738–746. [[CrossRef](#)]
39. Wisler, W.H. Conversion of bituminous coal to liquids and gases: Chemistry and representative processes. In *Magnetic Resonance: Introduction, Advanced Topics and Applications to Fossil Energy*; Springer: Dordrecht, The Netherlands, 1984; pp. 325–350.
40. Zhang, J.; Clennell, M.B.; Liu, K.; Dewhurst, D.N.; Pervukhina, M.; Sherwood, N. Molecular dynamics study of CO₂ sorption and transport properties in coal. *Fuel* **2016**, *177*, 53–62. [[CrossRef](#)]
41. Düren, T.; Bae, Y.-S.; Snurr, R.Q. Using molecular simulation to characterise metal–organic frameworks for adsorption applications. *Chem. Soc. Rev.* **2009**, *38*, 1237–1247. [[CrossRef](#)]
42. Liu, Z.-X.; Feng, Z.-C. Theoretical study on adsorption heat of methane in coal. *J. China Coal Soc.* **2012**, *37*, 647–653.
43. Wang, D. Study on Gas Adsorption and Diffusion of Soft and Hard Coal Based on Molecular Simulation. Master's Thesis, Henan Polytechnic University, Jiaozuo, China, 2018.
44. Krishna, R. Diffusion in porous crystalline materials. *Chem. Soc. Rev.* **2012**, *41*, 3099–3118. [[CrossRef](#)] [[PubMed](#)]
45. Kelemen, S.; Kwiatek, L. Physical properties of selected block Argonne Premium bituminous coal related to CO₂, CH₄, and N₂ adsorption. *Int. J. Coal Geol.* **2009**, *77*, 2–9. [[CrossRef](#)]
46. Hu, H.; Du, L.; Xing, Y.; Li, X. Detailed study on self-and multicomponent diffusion of CO₂-CH₄ gas mixture in coal by molecular simulation. *Fuel* **2017**, *187*, 220–228. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.