

Article

Competitive Adsorption Behavior of CO₂ and CH₄ in Coal Under Varying Pressures and Temperatures

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Abstract: The CO₂ injection technology for replacing CH₄ to enhance coalbed methane (CBM) recovery (CO₂-ECBM) offers dual benefits, i.e., reducing CO₂ emissions through sequestration and increasing CBM recovery, thereby leading to economic gains. However, there is no clear consensus on how temperature and pressure affect the competitive adsorption characteristics of CO₂ and CH₄ mixed gases in coal. Therefore, the competitive adsorption behavior of CO₂ and CH₄ mixed gases at various pressures and temperatures were investigated using the breakthrough curve method. Anthracite was selected for the adsorption experiment conducted under three gas injection pressure levels (0.1 MPa, 0.5 MPa, and 1 MPa) and at three temperature levels (20 °C, 40 °C, and 60 °C). This study showed that, when the temperature remained constant and the pressure ranged from 0.1 to 1 MPa, the adsorption rates of CO₂ and CH₄ increased as pressure rose. Additionally, the selectivity coefficient for CO₂/CH₄ decreased with an increase in pressure, suggesting that higher pressures within this range are not conducive to the replacement efficiency of CH₄ by CO₂. As the temperature increased from 20 to 60 °C under constant pressure conditions, both the selectivity coefficients for CO₂/CH₄ and the adsorption rates of CO₂ and CH₄ exhibited a downward trend. These findings imply that, within this temperature range, a reduced temperature improves the ability of CO₂ to efficiently displace CH₄. Moreover, CO₂ exhibits a higher isosteric heat of adsorption compared to CH₄.



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Keywords: coal; competitive adsorption; breakthrough curve; pressure; temperature

1. Introduction

Coal has served as a primary energy source worldwide and has been fundamental to the development of essential energy infrastructure, playing a crucial role in supporting global economic development [1]. As a form of nontraditional natural gas, coalbed methane (CBM) consists mainly of methane (CH₄) and is predominantly stored within coal seams [2]. To address the challenge of utilizing CBM stored in coal seams in a rational, efficient, and environment-friendly manner, the technology of injecting carbon dioxide (CO₂) to enhance CBM recovery (CO₂-ECBM) has been increasingly favored by scholars. Substituting CO₂ for CH₄ in the CO₂-ECBM technology facilitates CBM recovery, while reducing greenhouse gas emissions. Additionally, this method improves CBM recovery and yields greater economic benefits than environmental advantages [3,4]. Despite the widespread recognition of the CO₂-ECBM concept and its potential for CO₂ storage in coal seams, its large-scale implementation has progressed slowly [5]. Many critical questions remain unanswered, such as those pertaining to the cost–benefit analysis of CO₂ capture, transportation, and

injection, as well as how to optimize injection strategies to enhance CH₄ recovery rates and CO₂ storage efficiency.

Studies have demonstrated that coal exhibits varying adsorption capabilities for different gases [6,7]. Through experiments at different temperatures and pressures [8], Zhu et al. examined the adsorption capacities of three pure gases (CO₂, CH₄, and N₂) on three types of coal. Experiments on the adsorption of pure gases revealed that the adsorption capacities of different gases decreased with increasing temperature, with CO₂ exhibiting a significantly higher adsorption capacity than both CH₄ and N₂. Investigations have been carried out regarding the competitive adsorption of gas mixtures in coal. Yu et al. conducted single-component gas adsorption experiments on CH₄ and CO₂ at 28 °C and predicted the adsorption capacities of gas mixtures with compositions of 25% CO₂ + 75% CH₄, 65% CO₂ + 35% CH₄, and 85% CO₂ + 15% CH₄, using single-component adsorption isotherm model parameters [9]. The results showed that the gas mixtures exhibited adsorption capabilities that were between those observed for pure CO₂ and CH₄. Huang et al. conducted experiments on CO₂ and CH₄ mixed gases in three different ratios (1:3, 2:2, and 3:1), demonstrating that the adsorption capacities of these mixed gases conformed to this rule [10].

The selectivity of CO₂/CH₄ is another significant factor for competitive adsorption in coal. This coefficient is used to evaluate the effectiveness of replacing a weak adsorbate gas with a strong adsorbate gas [11,12]. Most current studies indicate that the adsorption selectivity of CO₂/CH₄ is greater than 1 when CO₂ and CH₄ mixed gases compete for adsorption in coal or shale [13–15]. Bai et al. created a molecular model of anthracite coal and performed the competitive adsorption simulations of CO₂ and CH₄ mixed gases at a constant temperature of 298 K and pressure ranging from 0.1 MPa to 5 MPa [16]. Molecular simulations revealed that the selectivity of CO₂/CH₄ decreased as the pressure increased. Zhang et al. conducted competitive adsorption experiments with different ratios of CO₂ and CH₄ mixed gases (25% CO₂ + 75% CH₄, 50% CO₂ + 50% CH₄, and 75% CO₂ + 25% CH₄) and arrived at the same conclusion [17]. Tao et al. applied the Monte Carlo method to study the adsorption selectivity of CO₂/CH₄ in coal, setting a temperature range between 278 and 398 K [18]. The results showed that the selectivity of CO₂/CH₄ decreased as the pressure increased from 0 MPa to 6 MPa, remained constant at a pressure between 6 MPa and 10 MPa, and decreased with temperature. Jia et al. conducted molecular simulations and found that the adsorption selectivity of CO₂/CH₄ initially increases and then decreases with the increase in pressure [19]. Li et al. developed three coal molecular models with different coal steps, demonstrating that the selectivity of CO₂/CH₄ decreased as the number of coal steps increased [20]. Guang et al. conducted competitive adsorption experiments of CO₂ and CH₄ mixed gases on coal at different steps, further discovering that the adsorption selectivity exhibits an asymmetric inverse parabolic trend with pressure for coal rank from coking coal to anthracite coal ($R_{o,max} > 1.78\%$), and for gas coal, long-flame coal, and lignite ($R_{o,max} < 1.78\%$), the adsorption selectivity follows a general decreasing tendency with the increase in pressure [21]. The study by Zhang et al. revealed that higher-order coal exhibited a higher selectivity for CO₂/CH₄ due to its better-developed microstructure and pore characteristics [22]. Molecular simulation technology provides an effective study method for studying the competitive adsorption behavior of gas mixtures in coal [23]. Owing to the limitations of molecular simulation technology and sophisticated coal molecules [24], the reliability of molecular simulation results still needs to be verified by experimental results.

Overall, Chinese and international researchers have made significant contributions to our understanding of the competitive adsorption characteristics of gas mixtures in coal. However, the details of the competitive adsorption process are not well understood,

and there is no unified understanding of the effects of temperature and pressure on the competitive adsorption process of mixed gases in coal. Therefore, this study aims to reveal the dynamic process of competitive adsorption of CO₂ and CH₄ mixed gases in coal using the breakthrough curve method and to analyze how pressure and temperature influence this competitive adsorption process, further understanding the competitive adsorption mechanism of mixed gases in coal.

2. Materials and Methods

2.1. Coal Sample

Anthracite was picked from the underground mining face of the Shanxi Chengzhuang mine and transported to the laboratory in sealed bags. After removing the surface layer of the coal sample in the laboratory, the samples were mechanically crushed and sieved to a particle size of 60–80 mesh. Subsequently, the processed samples were sealed and stored in self-sealing bags for use in subsequent experiments. The experimental coal samples were analyzed in accordance with the Elemental Analysis of Coal (GB/T 31391-2015) [25] and the Industrial Analysis Method of Coal (GB/T 212-2008) [26]. The pore structure of the coal sample was also evaluated in a previous study [27]. The results of the analysis are presented in Tables 1 and 2.

Table 1. The results of the elemental and industrial analyses of the coal sample.

Analysis Results	Surveillance Project	Proportion (%)
Elemental analysis	C _{ad}	77.59
	H _{ad}	2.84
	O _{ad}	3.48
	N _{ad}	1.21
	S _{ad}	0.24
Industrial analysis	M _{ad}	0.72
	A _{ad}	13.88
	V _{ad}	7.54
	FC _{ad}	77.86

Table 2. The pore parameters of the coal sample.

Pore Diameter (nm)	Pore Volume (cm ³ /g)	Specific Surface Area (m ² /g)
$d \leq 2$	0.0515	160.06
$2 \leq d \leq 50$	0.0777	54.42
$d > 50$	0.0053	0.0381

2.2. Experimental Methods

Competitive adsorption experiments were performed using a Multi-Constituent Adsorption Breakthrough Curve Analyzer (model BSD-MAB; Beishide Instrument Technology Co., Ltd., Beijing, China). Additionally, an online mass spectrometer (MS) (INFICON, Hamburg, Germany) was connected to the system to monitor the gas concentration at the outlet of the breakthrough column in real time.

The experimental protocol for the competitive adsorption of mixed gases is outlined as follows:

- (1) The coal sample was set in a drying cabinet at 100 °C for a predetermined drying time.
- (2) A 25 mL penetrating column with an inner diameter of 10 mm was selected. Quartz asbestos was inserted at one end of the column, followed by filling of the column with

the coal sample. Quartz asbestos was then added to the other end. Once loaded, the column was placed into the heating furnace.

- (3) Helium was purged into the penetrating column at a flow rate of 10 mL/min. First, the vacuum meter was heated by setting the temperature to 100 °C for 2 h. Subsequently, in situ heating was activated under atmospheric pressure for 30 min.
- (4) The four-way valve was adjusted and the CO₂ and CH₄ mixed gas concentrations were set to equal proportions. For the experimental procedures, temperatures of 20, 40, and 60 °C were employed. The pressure was set to 0.1, 0.5, and 1 MPa. The zero-concentration signal was identified using the MS, with no gas passing through the penetration column. Once the MS signal stabilized, the four-way valve was switched to allow gas to pass through the penetration column. After completing the gas concentration test, mass spectrometry detection was stopped while the gas flow and valve were closed.

2.3. Data Processing

Figure 1 illustrates the competitive adsorption breakthrough curves for a two-component mixed-gas system [28]. The “gas 1” curve shows the ratio of outlet to inlet concentration for the strongly adsorbed gas, while the “gas 2” curve illustrates the corresponding ratio for the weakly adsorbed gas. The areas labeled $S_1 + S_2$ represent the adsorption region for “gas 1”, while the area labeled $S_3 - S_1$ represents the adsorption region for “gas 2” in the breakthrough curve. These areas indicate the adsorption capacities for “gas 1” and “gas 2” as follows:

$$n_{\text{ads1}} = \frac{F \cdot y_1 \cdot \int_0^{t_1} \left(1 - \frac{C_1(t_1)}{C_0}\right) dt}{m} = \frac{F \cdot y_1 \cdot (S_1 + S_2)}{m} \quad (1)$$

$$n_{\text{ads2}} = \frac{F \cdot y_2 \cdot \int_0^{t_2} \left(1 - \frac{C_2(t_2)}{C_0}\right) dt}{m} = \frac{F \cdot y_2 \cdot (S_3 - S_1)}{m} \quad (2)$$

where n_{ads1} and n_{ads2} denote the dynamic adsorption capacities of the gas components (mL/g); F is the volumetric flow of the mixed gas (mL/min); y_1 and y_2 are the mole fractions of the two gases; C_1 and C_2 are the outlet concentrations of the two gases; C_0 is the inlet concentration of the two gases; t_1 and t_2 are the breakthrough time of the two gases; and m represents the mass of the adsorbent (g).

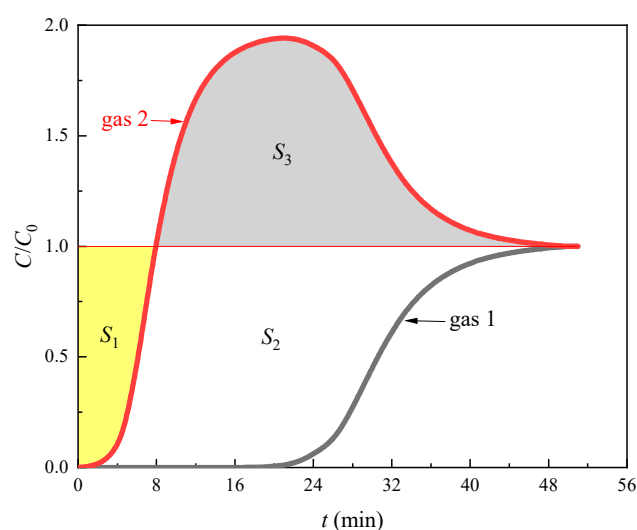


Figure 1. Breakthrough curves for typical binary mixed gases.

In this study, the adsorption selectivity coefficient of CO₂/CH₄ was determined using the following formula [29]:

$$\alpha = \frac{n_{\text{ads1}}/n_{\text{ads2}}}{y_1/y_2} \quad (3)$$

Equal volume fractions were assigned to CO₂ and CH₄, indicating that α represents the ratio of the adsorption areas of “gas 1” and “gas 2” in the breakthrough curve.

$$\alpha = \frac{S_1 + S_2}{S_3 - S_1} \quad (4)$$

An adsorption selectivity coefficient of >1 indicates that “gas 1” can displace “gas 2”, with higher values of “gas 1” being more effective in displacing “gas 2”.

Furthermore, the breakthrough point and the difference in the breakthrough time between the gas components were analyzed. The breakthrough point was defined as the time at which the outlet concentration of the gas component in the breakthrough curve reached 5% of the inlet concentration [30]. This parameter indicates the mass transfer rate of the gas component, as demonstrated by its position on the curve. The smaller the breakthrough point, the faster the breakthrough of the gas component occurred, indicating a higher mass transfer rate. The difference in the breakthrough time between gas components represents the time elapsed between the entry of different gases into the device and the first instance when their concentration reached the breakthrough point at the outlet end [31]. A greater difference in the breakthrough time corresponded to a more significant variation in the adsorption capacity of the two gas components on the adsorbent material.

2.4. Theoretical Modeling

2.4.1. Kinetic Model of Adsorption

The adsorption rate represents the gas adsorption capacity over a unit of time. In this study, the Bangham adsorption kinetic model was used to describe the adsorption rate results. The Bangham equation is expressed as follows [32]:

$$n_t = n_e \left(1 - e^{-k_b t^z}\right) \quad (5)$$

where n_t is the adsorption capacity at time t (mL/g), t indicates the adsorption time (min), z denotes the constant, k_b refers to the Bangham adsorption velocity constant (min^{−1}), and n_e is the adsorption capacity at equilibrium.

The adsorption rate is obtained by differentiating the Bangham equation, as follows:

$$\frac{dn_t}{dt} = k_b z t^{z-1} \cdot (n_e - n_t) \quad (6)$$

2.4.2. Adsorption Heat

Under conditions of low pressure, gas adsorption follows the principles of Henry’s law [33]. The mathematical expression for Henry’s law is expressed as follows:

$$n = Kp \quad (7)$$

where n represents the adsorbed capacity of the gas, K indicates Henry’s law constant, and p refers to the gas pressure.

The Van’t Hoff equation provides a means to determine the isosteric heat of adsorption ($q_{\Delta H}$), which can be represented mathematically as follows [34]:

$$q_{\Delta H} = \frac{dK}{dT} \frac{RT^2}{K} = -R \frac{d \ln K}{d(1/T)} \quad (8)$$

where K is the Henry's law constant, T is the absolute temperature, and R is the universal gas constant.

Plotting $\ln K$ against $1/T$ based on the Van't Hoff equation reveals the slope of the resulting line corresponding to $-q_{\Delta H}/R$. The Virial expansion equation was employed to compute the Henry's law constant (K) [35]. The Virial expansion equation is expressed as follows:

$$\ln\left(\frac{n}{p}\right) = z_0 + z_1n + z_2n^2 + z_3n^3 + \dots \quad (9)$$

where z_0 , z_1 , z_2 , and z_3 are the virial coefficients, and $K = \exp(z_0)$. When the adsorption capacity is significantly small, the third term and higher-order terms in the Virial equation are negligible, simplifying the equation as follows [36]:

$$\ln\left(\frac{p}{n}\right) = -z_0 - z_1n \quad (10)$$

By plotting $\ln(p/n)$ against n , the z_0 can be determined from the negative intercept of the resulting line.

3. Results and Discussion

3.1. Competitive Adsorption Breakthrough Curves

Figure 2 shows the breakthrough curves at different pressures and temperatures. Table 3 summarizes the breakthrough experimental parameters obtained from the tests. Table 3 indicates that, under equivalent pressure and temperature conditions, CH_4 consistently reaches its breakthrough point earlier than CO_2 , indicating that coal exhibits stronger adsorption selectivity for CO_2 . Figure 2a–f show that the breakthrough curves for CO_2 consistently demonstrate an initial phase where the relative concentration (C/C_0) remains zero. After a certain period, the CO_2 breakthrough curve gradually increases. Finally, when the relative concentration (C/C_0) reaches 1, it remains stable. The overall trend of the CH_4 breakthrough curve illustrates that the ratio of the CH_4 outlet concentration to the inlet concentration increases rapidly from 0 at the beginning. The concentration continues to increase until the outlet concentration equals the inlet concentration. Once the relative concentration (C/C_0) approaches 2, the curve begins to slow down, forming a bulge in the image [37]. Finally, the relative concentration (C/C_0) decreases to near 1 and remains stable. Owing to the replacement effect of CO_2 on CH_4 , the outlet concentration of CH_4 exceeds its inlet concentration, forming a raised peak in the graph. Once both CO_2 and CH_4 reach adsorption saturation, the ratio of their outlet concentration to inlet concentration begins to approach 1.

Figure 2a–c and Table 3 illustrate that, as temperature rises while pressure remains constant, the breakthrough points for both CO_2 and CH_4 and the difference in the breakthrough time exhibit a downward trend. This indicates that a higher temperature inhibits the adsorption of mixed gas in coal, with the effect on CO_2 being stronger than that on CH_4 . Figure 2d–f and Table 3 illustrate that, as pressure rises while temperature remains steady, the breakthrough points for both CO_2 and CH_4 and the difference in the breakthrough time exhibit an upward trend. This suggests that a higher pressure enhances the adsorption of mixed gas in coal, with a more pronounced effect on CO_2 than on CH_4 .

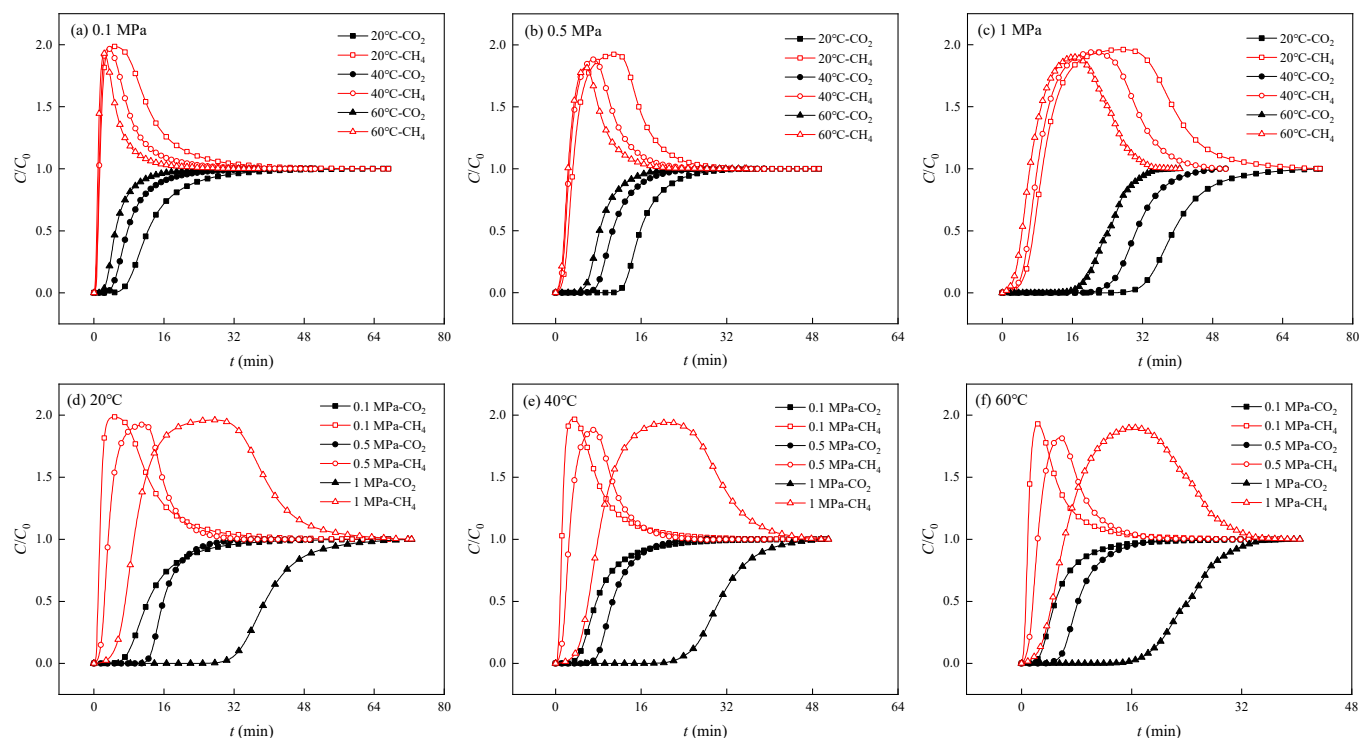


Figure 2. Breakthrough curves for CO₂ and CH₄ at various pressures and temperatures: (a) breakthrough curves at 0.1 MPa; (b) breakthrough curves at 0.5 MPa; (c) breakthrough curves at 1 MPa; (d) breakthrough curves at 20 °C; (e) breakthrough curves at 40 °C; and (f) breakthrough curves at 60 °C.

Table 3. Breakthrough experimental parameters for CO₂ and CH₄ adsorption.

Pressure (MPa)	Temperature (°C)	Gas Component	Breakthrough Point (min)	Breakthrough Time Difference (min)
0.1	20	CH ₄	0.485	6.602
		CO ₂	7.087	
	40	CH ₄	0.367	3.773
		CO ₂	4.140	
	60	CH ₄	0.210	2.358
		CO ₂	2.568	
0.5	20	CH ₄	1.038	11.629
		CO ₂	12.667	
	40	CH ₄	0.707	6.956
		CO ₂	7.663	
	60	CH ₄	0.590	4.952
		CO ₂	5.542	
1	20	CH ₄	3.677	27.946
		CO ₂	31.623	
	40	CH ₄	3.125	20.470
		CO ₂	23.595	
	60	CH ₄	1.777	15.690
		CO ₂	17.467	

3.2. Adsorption Capacity and Rate

Figure 3 illustrates the time-dependent adsorption capacity curves of the two gases at the same pressure but at different temperatures. Figure 3 shows that the adsorption capacities of the two gases increases with time and stabilizes once equilibrium is reached.

As temperature rises under constant pressure conditions, the adsorption capacities for both CO₂ and CH₄ experience a concurrent decline.

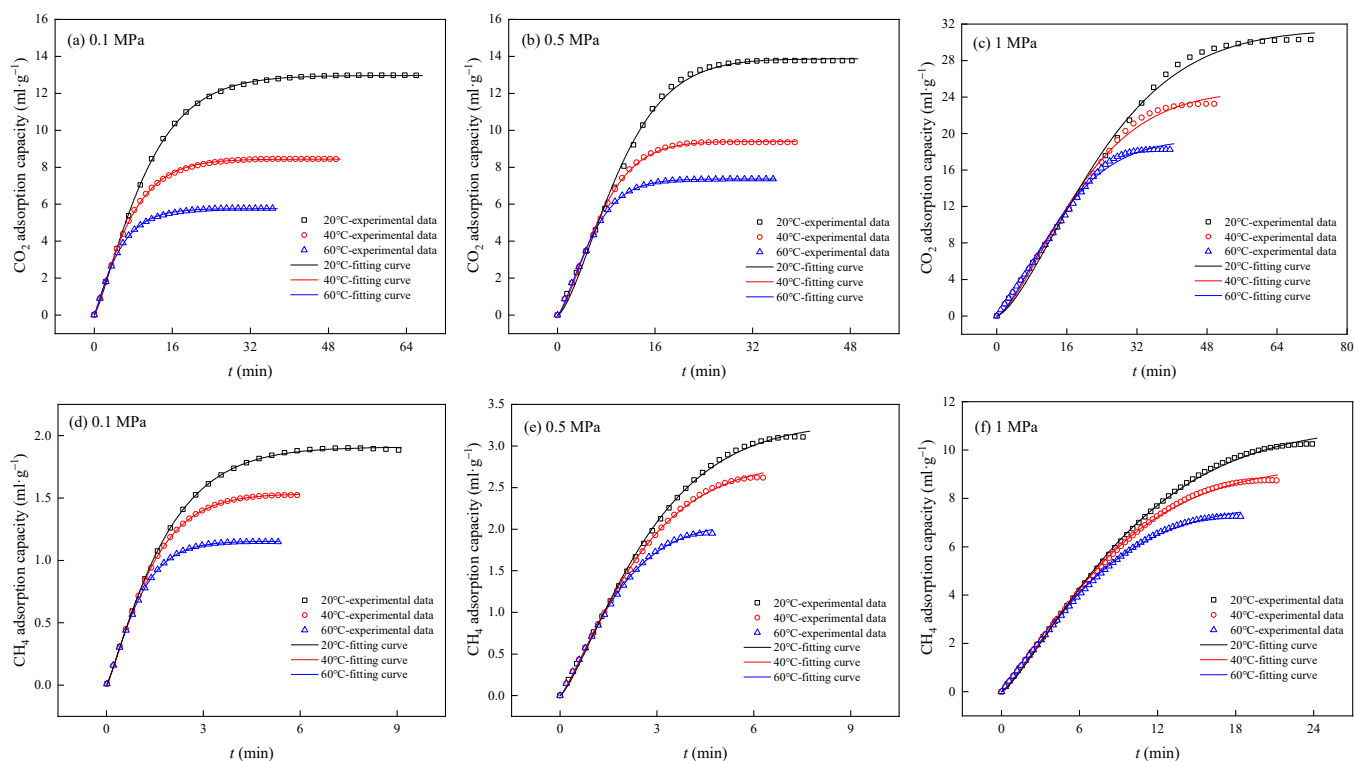


Figure 3. (a–c) Time-dependent adsorption capacity curves of CO₂. (d–f) Time-dependent adsorption capacity curves of CH₄.

To analyze the adsorption rate during the competitive adsorption process, the Bangham adsorption kinetics model was used for fitting. Figure 3 presents the fitting results, and Table 4 summarizes the corresponding fitted parameters. In Table 4, k_b represents the adsorption rate constant of the gas component. The Bangham model exhibits a remarkably strong fit to the experimental data, with the correlation coefficient (R^2) consistently surpassing 0.99.

The equilibrium adsorption capacities of the two gases at different pressures and temperatures are presented in Figure 4. Figure 4 demonstrates that the adsorption capacity of CO₂ exceeds that of CH₄ under identical temperature and pressure conditions. This observation is consistent with previous study findings [8–10]. This is attributed to the straight molecular geometry of CO₂ and the difference in electronegativity between carbon and oxygen, leading to a stronger quadrupole moment for CO₂. In contrast, the CH₄ molecule has a tetrahedral structure with a uniform electronegativity distribution and weaker polarity. Consequently, CO₂ molecules can potentially interact with polar sites (e.g., oxygen-containing functional groups of coal), thereby enhancing the adsorption capacity [38]. Additionally, the linear structure of the CO₂ molecule enables it to fill the pores of the adsorbent better, further enhancing the adsorption efficiency. At a constant temperature, the adsorption capacities of CO₂ and CH₄ increase as pressure increases, with a more significant increase observed in the 0.5–1 MPa range than in the 0.1–0.5 MPa range. As temperature rises under constant pressure conditions, the adsorption capacities of the two gases show a decline. The observed decline could be a result of the temperature-induced enhancement in the kinetic energy of the gas molecules. As gas molecules gain kinetic energy, they are more likely to desorb from adsorption sites.

Table 4. Fitting parameters of the Bangham model.

Pressure (MPa)	Temperature (°C)	Gas Component	n_e (mL/g)	k_b (min ^{−1})	z	R^2
0.1	20	CO ₂	12.9654	0.0482	1.2448	0.9998
		CH ₄	1.9072	0.4851	1.1760	0.9998
	40	CO ₂	8.4388	0.0883	1.1918	0.9998
		CH ₄	1.5325	0.6441	1.2215	0.9998
	60	CO ₂	5.7627	0.1489	1.1234	0.9995
		CH ₄	1.1545	0.9085	1.2383	0.9997
0.5	20	CO ₂	13.8577	0.0257	1.5032	0.9979
		CH ₄	3.2790	0.2421	1.3009	0.9988
	40	CO ₂	9.3935	0.0509	1.4422	0.9988
		CH ₄	2.8104	0.2978	1.2639	0.9990
	60	CO ₂	7.3626	0.0786	1.3833	0.9994
		CH ₄	2.2912	0.4297	1.2761	0.9987
1	20	CO ₂	31.3332	0.0070	1.5077	0.9959
		CH ₄	11.0565	0.0485	1.2899	0.9990
	40	CO ₂	24.6431	0.0109	1.4785	0.9957
		CH ₄	9.4067	0.0597	1.2873	0.9991
	60	CO ₂	19.3309	0.0157	1.4747	0.9956
		CH ₄	7.8680	0.0778	1.2496	0.9991

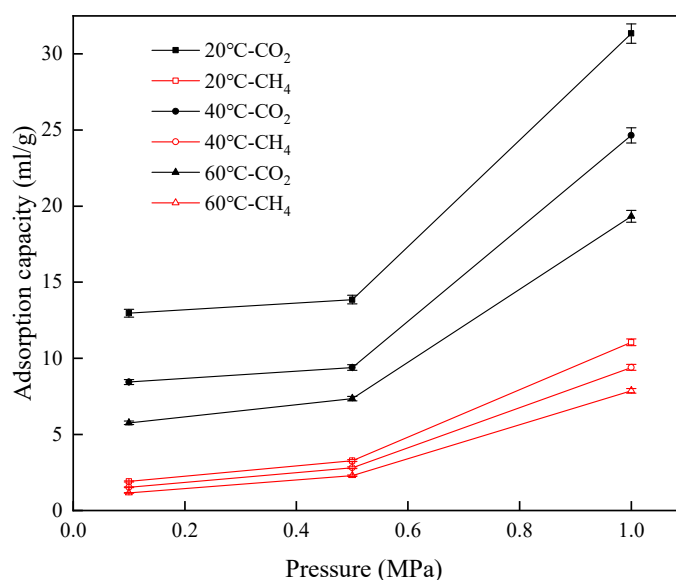


Figure 4. Equilibrium adsorption capacities of two gases at different pressures and temperatures.

A statistical significance test is conducted on the fitted adsorption capacities of the two gases [39]. A two-way ANOVA was performed using the Origin software v9.6.5.169 to analyze the effects of temperature and pressure on the adsorption capacities of CO₂ and CH₄. The results are shown in Table 5. The results indicated that, at the 0.05 significance level, the p -value for temperature of CO₂ was 0.00563, and the p -value for pressure of CO₂ was 3.42924×10^{-4} . Furthermore, at the 0.05 significance level, the p -value for temperature of CH₄ was 0.09525, and the p -value for pressure of CH₄ was 2.6889×10^{-4} . From these results, it can be concluded that temperature has a more significant impact on the adsorption capacity of CO₂ than on the adsorption capacity of CH₄, while pressure has a more significant impact on the adsorption capacity of CH₄ than on the adsorption capacity of CO₂.

Table 5. Overall analysis of variance (ANOVA).

Source	Gas Component	Degrees of Freedom	Sum of Squares	Mean Square	F-Value	p-Value
Temperature	CO ₂	2	111.86335	55.93167	24.66437	0.00563
	CH ₄	2	4.04936	2.02468	4.48049	0.09525
Pressure	CO ₂	2	480.76329	240.38164	106.00188	3.42924×10^{-4}
	CH ₄	2	108.42316	54.21158	119.967	2.6889×10^{-4}
Interaction	CO ₂	4	592.62664	148.15666	65.33313	6.74953×10^{-4}
	CH ₄	4	112.47251	28.11813	62.22375	7.42604×10^{-4}
Error	CO ₂	4	9.07084	2.26771	-	-
	CH ₄	4	1.80755	0.45189	-	-
Total	CO ₂	8	601.69748	-	-	-
	CH ₄	8	114.28006	-	-	-

To compare the variations in the adsorption capacities of the two gases with temperature and pressure, the relative reduction in the adsorption capacities was calculated as the temperature increased from 20 °C to 60 °C at a constant pressure. Additionally, the relative increase in the adsorption capacities was calculated as the pressure increased from 0.1 MPa to 1 MPa while maintaining a constant temperature. Table 6 presents the results of the calculations. Table 6 presents that, as the temperature rises from 20 °C to 60 °C at a constant pressure of 0.1 MPa, the adsorption capacity of CO₂ shows a significant decrease of 55.553%. In contrast, under the same conditions, the adsorption capacity of CH₄ exhibits a low reduction of 39.466%. A similar trend is observed at pressures of 0.5 MPa and 1 MPa.

Table 6. Changes in adsorption capacities at different temperatures and pressures.

Pressure (MPa)	Temperature Range (°C)	Gas Component	Relative Decrease in Adsorption Capacity (%)	Temperature (°C)	Pressure Range (MPa)	Gas Component	Relative Increase in Adsorption Capacity (%)
0.1	20–60	CO ₂	55.553	20	0.1–1	CO ₂	141.668
		CH ₄	39.466			CH ₄	479.724
0.5		CO ₂	46.870	40		CO ₂	192.021
		CH ₄	30.125			CH ₄	513.814
1		CO ₂	38.305	60		CO ₂	235.449
		CH ₄	28.838			CH ₄	581.507

As the pressure rises from 0.1 MPa to 1 MPa at a temperature of 20 °C, the adsorption capacity of CO₂ exhibits a 141.668% rise, while the adsorption capacity of CH₄ shows a more significant increase of 479.724%. Similarly, at 40 and 60 °C, the adsorption capacity of CH₄ exhibits a more substantial relative increase compared to that of CO₂.

Figure 5 illustrates the adsorption rate constants (k_b) for various gas components. Figure 5 shows that, at a constant temperature, k_b of the two gases decreases as the pressure increases. In contrast, at a constant pressure, an increase in temperature leads to a higher k_b for both gases.

Figure 6 illustrates the time-dependent adsorption rate curves. The adsorption rate is dynamic, progressing as the adsorption rates of the two gases increase rapidly at first and then decrease gradually. At constant temperature and pressure, the initial adsorption rate for CH₄ is higher than that for CO₂. However, as time progresses, CO₂ begins to adsorb more rapidly than CH₄, and this trend persists for the duration of the adsorption

process. Specifically, CO₂ exhibits a higher peak adsorption rate compared to CH₄. Table 4 shows that, at the same pressure and temperature, k_b of CH₄ exceeds that of CO₂. Based on the Bangham model, the adsorption rate is influenced by k_b and the adsorption capacity of the gas. Despite CH₄ having a higher k_b than CO₂, the adsorption capacity of CO₂ is considerably greater. Thus, CO₂ exhibits a faster adsorption rate compared to CH₄. As illustrated in Figure 6, when pressure remains constant, the adsorption rates of CO₂ and CH₄ decline more rapidly at higher temperatures. As temperature rises at a fixed pressure, the adsorption capacities of the two gases show a downward trend, while their k_b values simultaneously increase. The adsorption rates of the two gases decrease at elevated temperatures due to a reduction in adsorption capacity. Additionally, Figure 6 demonstrates that, as the pressure increases, the decline in the adsorption rates of the two gases becomes less pronounced. As the temperature remains constant, the adsorption capacities of the two gases increase with the rise in pressure, while their k_b values decrease. The adsorption rates of the two gases exhibit an upward trend with the increase in pressure, attributed to the enhancement in adsorption capacity.

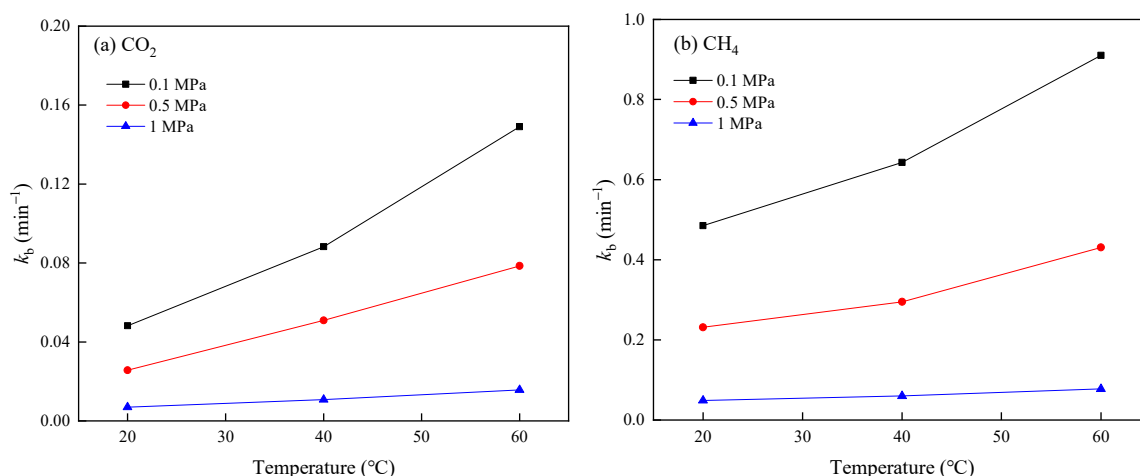


Figure 5. Adsorption velocity constants (k_b) of (a) CO₂ and (b) CH₄ at various conditions.

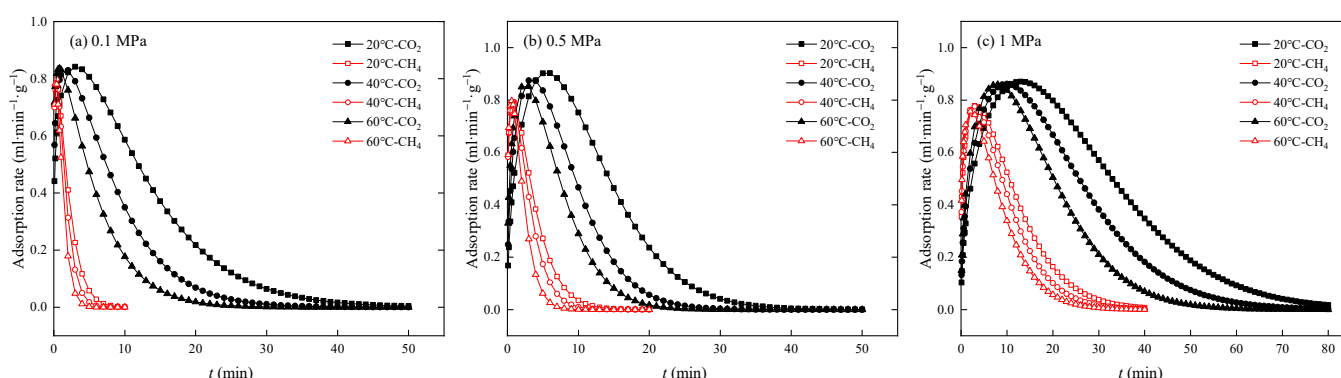


Figure 6. Time-dependent adsorption rate curves of CO₂ and CH₄ at (a) 0.1 MPa, (b) 0.5 MPa, and (c) 1 MPa.

According to the experimental results in 3.1 and the analysis of adsorption capacity and rate, the competitive adsorption and displacement process of CO₂ and CH₄ in coal can be deduced. CO₂ and CH₄ compete for adsorption sites on the coal surface, and due to its stronger adsorption capacity, CO₂ preferentially occupies the adsorption sites. As the adsorption capacity of CO₂ increases, it gradually displaces the already adsorbed CH₄, resulting in a bulge in the breakthrough curve of CH₄. The increase in temperature leads to a reduction in the adsorption capacity of both CO₂ and CH₄, with the decrease in

adsorption of CO₂ being more significant than that of CH₄. Additionally, the adsorption rates of both two gases decrease, and the effectiveness of CO₂ in displacing CH₄ diminishes, causing the bulge in the breakthrough curve of CH₄ to decrease. Contrarily, an increase in the pressure leads to an increase in the adsorption capacity of both CO₂ and CH₄, with the increase in adsorption of CO₂ being less pronounced than that of CH₄. Moreover, the adsorption rates of the two gases increase. During the pressure increase from 0.1 MPa to 0.5 MPa, the effect of increased adsorption capacity on the displacement of CH₄ by CO₂ is greater than the effect of increased adsorption rates, resulting in a decrease in the bulge of the breakthrough curve of CH₄. However, during the pressure increase from 0.5 MPa to 1 MPa, the effect of increased adsorption rates on the displacement of CH₄ by CO₂ surpasses the effect of increased adsorption capacity, leading to an increase in the bulge of the breakthrough curve of CH₄.

3.3. Analysis of Adsorption Selectivity

Figure 7 illustrates the changes in adsorption selectivity coefficients of CO₂/CH₄ under different pressures and temperatures, and the corresponding results of the adsorption selectivity are shown in Table 7. Table 7 and Figure 7 demonstrate that, under a constant temperature, the adsorption selectivity for CO₂/CH₄ shows an inverse relationship with the increase in pressure. In previous studies, some researchers have suggested that the adsorption selectivity coefficient for CO₂/CH₄ decreases with an increase in pressure [15,17], while others have proposed that the adsorption selectivity coefficient for CO₂/CH₄ initially increases and then decreases with a rise in pressure [19,21]. This indicates that the adsorption selectivity coefficient for CO₂/CH₄ varies differently with pressure for different types of coal [40]. As previously analyzed, the increment in pressure induces an increment in the adsorption capacity for both CO₂ and CH₄; however, the relative increment in the adsorption capacity of CH₄ is more significant than that of CO₂, leading to a decreased adsorption selectivity for CO₂/CH₄. At a constant pressure, the adsorption selectivity for CO₂/CH₄ shows a negative correlation with the rise in temperature. As previously analyzed, higher temperatures result in a reduction in the adsorption capacities of the two gases; however, the relative decrease in CO₂ exceeds that in CH₄, resulting in a decreased adsorption selectivity for CO₂/CH₄. Moreover, a rise in temperature could potentially reduce the specific surface area of coal's micropores [41]. Table 2 shows that the coal sample exhibits a high proportion of well-developed micropores ($d \leq 2$ nm). The decrease in the specific surface area of the micropores leads to fewer adsorption sites for gas molecules. CO₂, with its stronger adsorption selectivity, occupies more of these sites, contributing to a larger decrease in CO₂ in coal.

Table 7. Adsorption selectivity coefficients for CO₂ and CH₄ at varying pressures and temperatures.

Pressure (MPa)	Temperature (°C)	Adsorption Selectivity Coefficients for CO ₂ /CH ₄
0.1	20	6.798
	40	5.507
	60	4.992
0.5	20	4.226
	40	3.342
	60	3.213
1	20	2.834
	40	2.620
	60	2.457

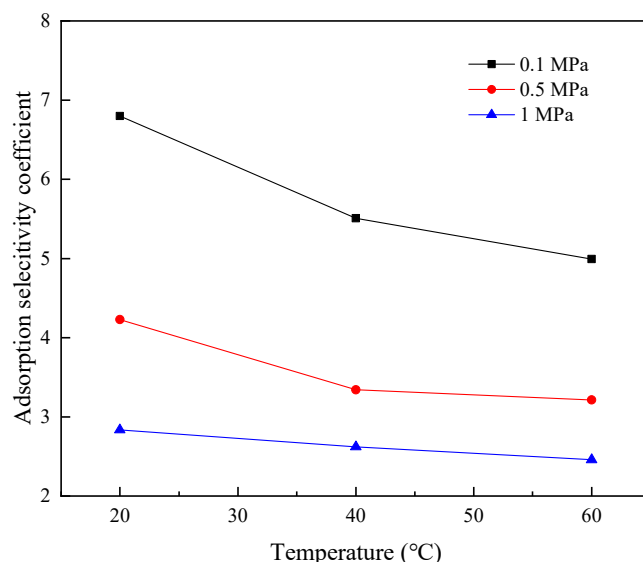


Figure 7. Adsorption selectivity coefficients for CO₂/CH₄ at different pressures and temperatures.

3.4. Thermodynamic Analysis of the Adsorption Process

Figure 8 illustrates the fitting curves of $\ln(p/n)$ versus n for the gas components at various temperatures, and Table 8 lists the corresponding parameters. Additionally, Figure 9 shows the fitted curve of $\ln K$ versus $1/T$, based on Henry's law constant (K). The isosteric heats of CO₂ and CH₄ were obtained from the slope of the fitted line. The isosteric heat values of CO₂ and CH₄ are 27.46 kJ/mol and 11.09 kJ/mol, respectively, suggesting that both gases undergo physical adsorption (<40 kJ/mol). The values are consistent with those reported in previous studies [19,21], and CO₂ exhibits a higher isosteric heat compared to CH₄. This is because, while CO₂ molecules are generally linearly symmetrical and non-polar, the electronegativity difference between the carbon and oxygen atoms during the adsorption process results in an uneven distribution of the electron cloud. During the adsorption process, CO₂ molecules may experience some polarity interactions with the adsorbent surface, whereas CH₄ molecules, with their completely symmetrical tetrahedral structure and uniform electronegativity distribution, lack polarity [42]. Additionally, the kinetic diameter of CO₂ molecules (0.33 nm) is smaller than that of CH₄ molecules (0.38 nm) [43]. This smaller molecular size allows CO₂ to penetrate deeper into the micropores and slits of the adsorbent, accessing more adsorption sites, thereby increasing the isosteric heat. A higher isosteric heat indicates that the adsorption process encounters significant energy barriers, potentially resulting in a lower adsorption rate during the initial stage. However, once adsorption begins, stronger interactions promote an increase in the adsorption rate. The adsorption capacity for CO₂ surpasses that of CH₄, with the adsorption selectivity coefficient of CO₂/CH₄ exceeding 1. This phenomenon correlates with the higher adsorption heat of CO₂ in comparison to that of CH₄. This finding suggests that CO₂ has advantages in the competitive adsorption.

Table 8. Fitting parameters of the Virial equation.

Gas Components	Temperature (°C)	Intercept	K (mmol·g ^{−1} ·MPa ^{−1})
CO ₂	20	−2.7583	15.7730
	40	−1.9674	7.1521
	60	−1.4088	4.0910
CH ₄	20	0.0472	0.9539
	40	0.2846	0.7523
	60	0.5969	0.5505

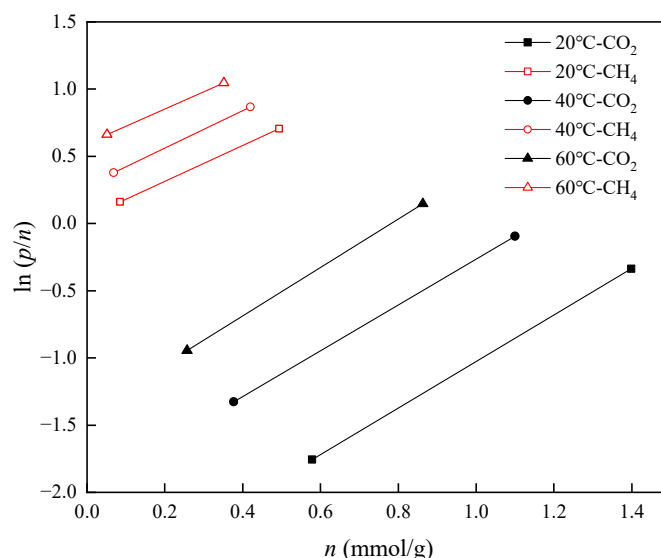


Figure 8. Fitting curve of $\ln(p/n)$ versus n for CO₂ and CH₄ adsorption.

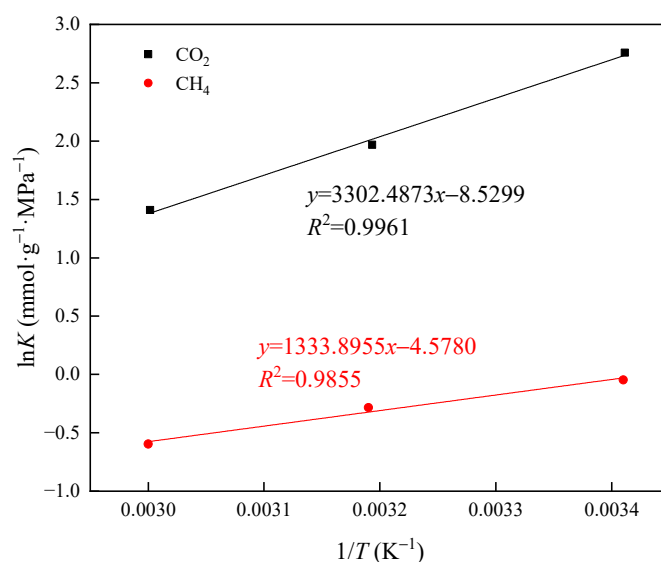


Figure 9. Relationship between $\ln K$ and $1/T$.

4. Conclusions

The optimization of CO₂ injection parameters to maximize the displacement effects of CO₂ on pre-adsorbed CH₄ is an urgent issue that needs to be addressed for the CO₂-ECBM technology. This study demonstrates the competitive adsorption process of CO₂ and CH₄ mixed gases in coal at various pressures and temperatures using the breakthrough curve method. The key conclusions that can be drawn are as follows:

- (1) At a constant temperature and within the pressure range of 0.1 MPa to 1 MPa, the adsorption capacities and rates of CO₂ and CH₄ increase with the increase in pressure. Additionally, the relative increase in the adsorption capacity of CH₄ exceeds that of CO₂, which results in the selectivity coefficient for CO₂/CH₄ decreasing with an increase in pressure, indicating that high pressure in the range of 0.1 MPa to 1 MPa is unfavorable for the replacement efficiency of CH₄ by CO₂.
- (2) At a constant pressure and within the temperature range of 20–60 °C, the adsorption capacities and rates of CO₂ and CH₄ decrease with the increase in temperature and the relative decrease in the adsorption capacity of CO₂ is greater than that of CH₄. Thus,

the selectivity coefficient for CO₂/CH₄ decreases as temperature rises, indicating that lower temperatures are beneficial to the replacement efficiency of CH₄ by CO₂.

- (3) The isosteric heat values of CO₂ and CH₄ are 27.46 kJ/mol and 11.09 kJ/mol, respectively, suggesting that both gases undergo physical adsorption. The isosteric heat value of CO₂ is greater than that of CH₄, which may be because CH₄ molecules lack polarity and have a larger molecular size compared to CO₂ molecules.
- (4) A higher isosteric heat indicates that the adsorption process encounters significant energy barriers, potentially resulting in the initial adsorption rate of CH₄ being higher than that of CO₂. As time progresses, CO₂ begins to adsorb more rapidly than CH₄, and this trend persists for the duration of the adsorption process.
- (5) In this study, only the operational conditions (temperature and pressure) were varied to evaluate their effects on the competitive adsorption behavior. Other factors, such as the composition ratio of mixed gases, specific surface area of coal, porosity, pore size, particle size, and moisture content, remain insufficiently understood.
- (6) To further improve the understanding of the competitive adsorption behavior of coal for gas mixtures, future studies should investigate the effects of modifying the composition ratio of CO₂ and CH₄, using different coal grades, or varying the moisture content of coal on the competitive adsorption characteristics.

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