Adsorption Characteristics of CH$_4$ and CO$_2$ in Shale at High Pressure and Temperature

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ABSTRACT: This work presents the adsorption behavior and appearance characteristics of CH$_4$ and CO$_2$ on the Longmaxi shale at high pressure and temperature. To investigate the variation of gas adsorption patterns under the constraint of pressure and temperature, the applicability of the theories of monolayer adsorption, multilayer adsorption, and micropore filling was discussed. The preferential selection coefficient of CO$_2$ for CH$_4$ under different conditions was characterized by the absolute adsorption capacity ($V_{ads}$) ratio of CO$_2$ to CH$_4$ ($\alpha$CO$_2$/CH$_4$). Moreover, the implication of the CO$_2$ injection to enhance gas recovery and the CO$_2$ capture and storage (EGR–CCS) process was analyzed. The results exhibit that the excess adsorption curves of CH$_4$ are smooth, and the experimental temperature has no noticeable effect on the shape of curves. At the same time, a “sharp peak” is recorded in the excess adsorption curves of CO$_2$ at low temperatures (30 and 55 °C) near the critical pressure, which is quite distinct from the smooth curves at high temperatures (80 and 100 °C). Correspondingly, there are two “jump pressure” values in the density curves (30 and 55 °C) of the adsorption system and the density curves are divided into three stages. The Dubinin–Astakhov and Brunauer–Emmett–Teller (BET) models show an optimum degree of fit for CH$_4$ and CO$_2$ adsorption curves under all experimental temperature and pressure conditions. The Langmuir model fits the adsorption curves of 80 and 100 °C better, while the BET model is appropriate for 30 and 55 °C. The adsorption affinity of CO$_2$ is higher than CH$_4$, with the value of $\alpha$CO$_2$/CH$_4$ in the range of 2.47–12.16. The value of $\alpha$CO$_2$/CH$_4$ increases with a rise in pressure but is inhibited by high temperatures, while the inhibition is negligible when the experimental temperature exceeds 80 °C. The adsorption preferential of CO$_2$ is stronger in the shallow reservoir ($\alpha$CO$_2$/CH$_4$ > 10.5), and the application prospect of the EGR process is promising. In contrast, the adsorption preferential is slightly weakened in the deep reservoir ($\alpha$CO$_2$/CH$_4$ < 4.5), which can be considered for CO$_2$ capture, utilization, and storage. Results from this investigation provide novel insights on the adsorption characteristics of CH$_4$ and CO$_2$ on the shale matrix at high pressure and temperature. They are also expected to give certain enlightenment for the EGR–CCS process.

1. INTRODUCTION

Shale gas is an unconventional clean energy source, with a wide distribution, having multiple strata and high reserves, and showing enormous development potential, and is receiving increasing attention worldwide.1−3 Shale with “low porosity and low permeability” limits its natural productivity. The stimulation effect of a traditional hydraulic fracturing technology is remarkable.3,4 However, a series of deficiencies need to be solved by alternative methods. For instance, the fracturing fluid may trigger a drop in the groundwater levels. The flowback gives rise to pollution, uncontrollable local earthquakes caused by the fracturing process, the mechanically complexity of the fracturing process, and the sensitivity of shale reservoirs to the fracturing fluid.5−7 Besides, the hydraulic fracturing technology is getting worse with the rise in burial depth, and the development cost is enormous. It is a significant factor limiting the commercial development of deep shale gas reservoirs. The research of a new clean stimulation technology is crucial for the development of deep shale gas reservoirs. On the other hand, CO$_2$ emission is the dominant proportion of global carbon, which caused a severe greenhouse effect. Emission reduction and even carbon neutralization have become the main target of atmospheric environmental protection in the world. CO$_2$ capture and storage (CCS) is a promising way to achieve CO$_2$ emission reduction, and the widely distributed shale reservoir is one of the potential geological bodies.8,9 CO$_2$ injection to reservoir enhanced gas recovery, and realized CO$_2$ CCS is a potential high-quality development project.3,10 Its essence is to inject CO$_2$ into the shale gas
reservoir, and CO$_2$ competes with CH$_4$ for adsorption sites on the shale matrix, which boosts CH$_4$ desorption and enhances the recovery. Meanwhile, the excellent sealing properties of shale allow for the storage of CO$_2$, thereby being mutually beneficial in improving shale gas recovery and alleviating global warming. The adsorption capacity and priority of CO$_2$ in shale are higher than that of CH$_4$, which is the basis of the exhaust gas recirculation (EGR)–CCS process.\textsuperscript{2,10} The proportion of adsorbed gas in shale is in the range of 20–85\%,\textsuperscript{11} so that its successful desorption is crucial to the stable production of shale gas reservoirs. The adsorption characteristics, controlling factors, and controlling mechanisms of CH$_4$ and CO$_2$ in shale have attracted extensive attention. There is an apparent impact of in situ temperature and pressure, mineral composition, organic matter content, and pore structure of the reservoir on the gas adsorption process.\textsuperscript{12,13} Wang et al.\textsuperscript{14} simulated the adsorption behavior of CH$_4$ (0–10 MPa at room temperature) in the Longmaxi and Niutitang shales using the Langmuir and Brunauer–Emmett–Teller (BET) models. Zhou et al.\textsuperscript{15} conducted the adsorption experiments of CH$_4$ and CO$_2$ (0–12 MPa, 35–55 °C), utilizing the Ono–Kondo and Dubinin–Astakhov (D–A) models. Abdul Kareem et al.\textsuperscript{16} performed the adsorption of CO$_2$ (0–15 MPa, room temperature). Bemani et al.\textsuperscript{17} and Eshkalak et al.\textsuperscript{18} carried out the adsorption of CO$_2$ and CH$_4$ on shale and discussed the superiority of CO$_2$ displacement of CH$_4$. Gu et al.\textsuperscript{18} investigated the relationship of $\alpha$CO$_2$/CH$_4$ versus mineral composition and pore structure in marine shale. Overall, the adsorption of CO$_2$ and CH$_4$ in shale is controlled mainly by temperature, pressure, mineral composition, and total organic carbon. The adsorption capacity of CO$_2$ and CH$_4$ increases gradually with a rise in pressure until the adsorption equilibrium is reached.\textsuperscript{15} Increasing temperature inhibited the adsorption, and the adsorption capacity decreased with a rise in temperature.\textsuperscript{15} The value of $\alpha$CO$_2$/CH$_4$ also increased with an increase in pressure and reduced with a rise in temperature.\textsuperscript{17,18}

However, the maximum experimental pressure of CO$_2$ and CH$_4$ adsorption mainly was less than 10 MPa in a previous work and rarely reached 15 MPa. Experimental pressures over 20 MPa were exceedingly rare. The exploitation of shale gas has been developed for deep reservoirs, where the reservoir pressure is greater than 20 MPa. Research on the adsorption behavior of CH$_4$ and CO$_2$ under high pressure is therefore lacking. Additionally, the experimental temperature of CO$_2$ and CH$_4$ was predominantly performed at room temperature. A few scholars discussed the influence of temperature on the adsorption behavior within a specific range, generally below 55 °C, but the maximum temperature of deep shale gas reservoirs is commonly over 100 °C. The research on CO$_2$ and CH$_4$ adsorption under high temperature is surprisingly limited, and the effect of temperature and pressure on $\alpha$CO$_2$/CH$_4$ also requires further investigation. Furthermore, the investigation of a proper model fitting of CO$_2$ and CH$_4$ adsorption under high pressure and temperature is lacking. Besides, it needs to be verified whether the appropriate models under low pressure and temperature also have a high degree of fit in high pressure and temperature. It is, therefore, necessary to perform the model fitting of the isothermal adsorption models for CO$_2$ and CH$_4$ under high pressure and temperature.

This investigation focused on the Longmaxi shale in south Sichuan, China, and simulated the adsorption behaviors of CH$_4$ and CO$_2$ under high pressure and temperature (30–100 °C, 0–25 MPa) through isothermal adsorption experiments. To explore the gas adsorption characteristics of deep shale gas reservoirs under in situ conditions and the variation of CO$_2$ adsorption superiority, the $V_{abs}$ was corrected by the $V_{ex}$. The Langmuir, BET, and D–A isothermal adsorption models were employed to fit the adsorption data of CH$_4$ and CO$_2$. The applicability of the models was evaluated using $R^2$ values as the standard of the degree of fit. The adsorption mechanism and primary occurrence pattern of CH$_4$ and CO$_2$ in shale were also discussed. Additionally, $\alpha$CO$_2$/CH$_4$ were calculated to analyze the preferential selection coefficient of CO$_2$ for CH$_4$ under different pressures and temperatures. The research results provide references for adsorption behaviors of CH$_4$ and CO$_2$ on shale and have theoretical significance for the promotion and development of the EGR–CCS process in shale gas reservoirs.

2. SAMPLE, EXPERIMENTS, AND METHODS

2.1. Sample Information. In this investigation, drilling cores of the Longmaxi Formation shale gas reservoir in the Changning area of the southern Sichuan Basin (Figure 1), one of the shale gas exploration and development demonstration

Figure 1. Schematic diagram of the sampling point tectonic location.
areas in China, are selected as the research objects. Four black organic-rich shale samples were collected from the lower part of the Longmaxi Formation in the Lower Silurian in Well X, which are YS-13, YS-14, YS-15, and YS-16 from bottom to top, and the corresponding burial depths are 1243.77–1244.04, 1241.74–1242.01, 1239.72–1239.99, and 1237.96–1238.23 m, respectively.

2.2. Isothermal Adsorption Experiments of CH₄ and CO₂. In this investigation, the ISOSORP-SC high-pressure isotherm adsorption instrument was employed to test the adsorption behavior of CH₄ and CO₂ by using the gravimetric method. The adsorption system consists of a control cabinet system and magnetic suspension balance system (Figure 2). The former can be used to transport adsorbate, vacuumize, and control experimental pressure. The latter completes the sample adsorption, temperature control, adsorption system parameters, and result recording. The experiments were conducted according to the standard of NB/T 10117-2018. Before the experiments, the shale samples were ground to 60–80 mesh. During the screening process, the particles less than 80 mesh should be fully screened out and each sample should weigh 10 g. The prepared samples were heated and dried in a vacuum at 110 °C for 12 h to remove the adsorbed water vapor. According to the adsorption requirements of CH₄ and CO₂, the gas path was connected, and the working state of the balance suspension system was checked after startup.

After the airtightness test, blank test, pretreatment experiment, and buoyancy test, the isothermal adsorption tests were exerted. Specific experimental details are as follows:

First, the CH₄ adsorption isotherm experiments were conducted. The experimental pressure was in the range of 0–25 MPa, 13 pressure points of 0, 2, 4, 22, and 24 MPa were designed totally and exerted at 30, 55, 80, and 100 °C (YS-16 at 30 °C, YS-15 at 55 °C, YS-14 at 80 °C, and YS-13 at 100 °C), respectively. The experimental temperature was controlled by a high-precision oil bath thermostat. After the CH₄ isothermal adsorption experiments at all four temperatures were complete, the samples were vacuumed at 110 °C for 12 h to remove the residual CH₄. After that, the abovementioned procedures were repeated to conduct the isothermal adsorption experiments for CO₂.

2.3. Correction of Adsorption Capacity. The test result of the isothermal adsorption experiment is excess adsorption capacity (V_ex), which is the excess capacity of the adsorption phase density that exceeds the bulk phase density. This is also known as the Gibbs adsorption capacity. During the calculation process, the volume of the adsorption phase is ignored, which leads to a calculated value that is lower than the actual adsorption capacity. It is, therefore, significant to correct the actual adsorption capacity. For this study, CH₄ and CO₂ will be transformed into the supercritical state (CO₂: 31.04 °C, 7.38 MPa; CH₄: −82.59 °C, 4.59 MPa). It is challenging to meet the requirements of the isothermal adsorption experiments at different temperatures by simply setting ρ_a as a constant. Therefore, scholars proposed that the V_ex will linearly decrease during the high-pressure stage. The bulk density can be taken as the absissa, and the V_ex in the descending section can be taken as the ordinate. The intercept of the fitting curve on the X-axis is ρ_a.

2.4. Fitting Models of the Adsorption Results. Monolayer adsorption, multilayer adsorption, and micropore filling theories are widely accepted in the research of gas adsorption behavior on solid adsorbent surfaces and the internal and external surfaces of porous media. To explore the adsorption pattern of CH₄ and CO₂ under different temperatures and pressures, the most representative isothermal adsorption model of the three theories was selected, which are the Langmuir model, BET model, and D–A model. The details of calculation principles and methods are as follows:

2.4.1. Langmuir Model. The Langmuir model is a widely accepted isotherm adsorption equation (eq 2). The Langmuir model assumes that the adsorption energy on the adsorbent surface is uniform and constant. Only a monolayer of adsorption is formed on the adsorbent surface, and the adsorption capacity reaches the maximum when the monolayer adsorption is saturated. Therefore, adsorption is a monolayer. Also, if the adsorption mechanism is equivalent, no
intermolecular force exists among the adsorbates, which means that only a gas molecule will be adsorbed at each adsorption site.

$$V_{abs} = \frac{V_{L}P}{P + P_{L}}$$  

where $P$ is the experimental pressure at adsorption equilibrium, MPa; $V_{L}$ is the Langmuir volume, cm$^3$/g, which represents the maximum adsorption capacity of a monolayer and is determined by the property of shale and the type of adsorbate; and $P_{L}$ is the Langmuir pressure, MPa, the value is the pressure when the adsorption capacity equals to $V_{L}/2$.

2.4.2. BET Model. The BET model was established by Brunauer et al., who expanded and extended the Langmuir model (eq 3) and concluded that physical adsorption is caused by the Van der Waals forces. This model states that the intermolecular force existed among the adsorbates due to the Van der Waals force of the gas molecules, thereby formed multilayer adsorption. The BET model assumes that the adsorption heat of the first layer is constant. The adsorption heat of each layer is equal to the condensation heat after the second layer, and the adsorption layers are infinite.

$$\frac{V_{abs}}{V_{m}} = \frac{c(p/P_{L})}{1 - \left(1 - c\left(\frac{P}{P_{L}}\right)\right)}$$  

Figure 3. $V_{ex}$, $V_{abs}$, and $V_{abs} - V_{ex}$ of CH$_4$ adsorption results on shale.

Figure 4. $V_{ex}$, $V_{abs}$, and $V_{abs} - V_{ex}$ of CO$_2$ adsorption results on shale.
where $V_m$ is the saturated adsorption capacity of a monolayer, $\text{cm}^3/g$; $p_0$ is the saturated vapor pressure at the experimental temperature, MPa; and $c$ is a constant, dimensionless, related to the adsorption heat.

2.4.3. D–R and D–A Models. The D–R model\textsuperscript{28} is based on the micropore filling theory and the Polanyi\textsuperscript{29} adsorption potential theory (eq 4), which is suitable for the adsorption behavior of gas molecules on the surface of porous adsorbents. It is suggested that the adsorption mechanism of gas on micropore adsorbents is quite distinct from that on open surfaces due to the small distances between the pore walls. The gas adsorption in the micropore fills the pores, different from the molecular layer adsorption described by the Langmuir and BET models. The D–A model (eq 5) amends the D–R model and has one more fitting parameter, which significantly enhances the flexibility.

$$V_{abs} = V_m \exp \left\{ -D \left\lfloor \ln \left( \frac{p_0}{P} \right) \right\rfloor \right\}$$

$$V_{abs} = V_m \exp \left\{ -D \left\lfloor \ln \left( \frac{p_0}{P} \right) \right\rfloor ^c \right\}$$

where $\alpha$ is the structural heterogeneity constant of shale, with a value in 1–4 ranges.

3. RESULTS AND DISCUSSION

3.1. $V_{abs}$ and $V_{ex}$. 3.1.1. Adsorption Results of CH$_4$. The morphology of the $V_{ex}$ curves of CH$_4$ in four samples is analogous and exhibits a convex shape (Figure 3). $V_{ex}$ increases fast from 0 to 4 MPa, and the increments gradually reduce with a rise in pressure (4–10 MPa). From 10 to 16 MPa, the $V_{ex}$ drops, and the slope gradually increases. For $V_{abs}$, the adsorption amount increases continuously with a rise in pressure until the adsorption equilibrium is reached. The discrepancy of $V_{abs}$ and $V_{ex}$ grows linearly with an increase in pressure. This is because the volume of the adsorbed phase is not accounted for and the larger the bulk density is, the discrepancy will be more significant with a rise in pressure.

3.1.2. Adsorption Results of CO$_2$. The $V_{ex}$ curves of CO$_2$ at different temperatures exhibit significant discrepancies (Figure 4). The experimental temperatures of YS-13 (100 °C) and YS-14 (80 °C) are higher, and the $V_{ex}$ curves are convex and smooth. $V_{ex}$ increases fast from 0 to 2 MPa, and adsorption incrementally reduces and increases linearly from 2 to 14 MPa. After that, $V_{ex}$ decreases linearly when $P > 16$ MPa. In contrast, the experimental temperatures of YS-15 (55 °C) and YS-16 (30 °C) are relatively lower. Although the $V_{ex}$ curves are also convex, a “sharp peak” (Figure 4) existed, distinct from the high-temperature curves. In previous studies, the characteristics of CO$_2$ excess adsorption curves can be divided into two categories: (i) type I adsorption isotherm in BDDT classification\textsuperscript{30} and (ii) typical CH$_4$ excess adsorption curves similar to Figure 3.\textsuperscript{15} The adsorption experiments were repeated three times and similar experimental phenomena were obtained. This indicates that the “sharp peak” of CO$_2$ excess adsorption curves at 30 and 55 °C is anomalous and should be deeply explored.

The “sharp peak” of excess adsorption curves on YS-15 (55 °C) and YS-16 (30 °C) approximately starts at 6 MPa and ends at 14 MPa and reaches the maximum at 10 MPa (Figure 4). Tsuzuki et al.,\textsuperscript{31} Yang et al.,\textsuperscript{32} and Nikolai et al.\textsuperscript{33} reported that when CO$_2$ is close to the critical state, the sensitivity of compressibility to pressure change is significantly improved, and the aggregation behavior is remarkable; and when far away from the critical pressure, the state of CO$_2$ tends to stable again. The tiny change of pressure will have a significant impact on the density and viscosity of CO$_2$ nearing the critical pressure. The characteristics of density variation in the adsorption system during the adsorption of CH$_4$ and CO$_2$ were analyzed (Figure 5). The curves of CH$_4$ density versus experimental pressure are characterized by a “single stage”, which is determined by the thermodynamic and transport properties of CH$_4$. It is a gradual system in the adsorption process, corresponding to the smooth and continuous characteristics of CH$_4$ excess adsorption curves in Figure 3. In contrast, the density curves of CO$_2$ of YS-13 (100 °C) and YS-14 (80 °C) are characterized by “double stages”, and the “jump pressure” is about 7 MPa, nearing the critical pressure. For YS-15 and YS-16, the experimental temperature is relatively close to the critical temperature of CO$_2$, and the density curves are characterized by “ternary stages” separated by two “jump pressure” values (Figure 5). Namely, CO$_2$ is in a subcritical state (0–7 MPa), the compressibility is relatively lower, resulting in a slow rise in the correlation curves of density versus experimental pressure in stage ①. Then, the property of CO$_2$ becomes active nearing the critical pressure. The sensitivity of compressibility and density to pressure increases significantly, resulting in a sharp rise in the slope of stage ②. When the pressure is far away from the critical pressure, CO$_2$ transforms into a stable supercritical state. The sensitivity of compressibility and density to the pressure becomes steady, resulting in a slower slope of the density curves of stage ③ (Figure 5). In addition, although the experimental temperature of YS-16 is 30 °C, which is slightly lower than the critical temperature of CO$_2$, Yang et al.\textsuperscript{32} and Nikolai et al.\textsuperscript{33} suggested that the CO$_2$ properties also change significantly when it approaches the critical temperature. Overall, the adsorption capacity and density of the CO$_2$ are obviously decreased at high temperature, especially when CO$_2$ is in a supercritical state, the regularity is more prominent, which is consistent with the current general understanding.
3.2. Model Fitting of the Adsorption Behaviors. In Figures 3 and 4, the $V_{abs}$ curves of CH$_4$ and CO$_2$ (especially the latter one) at different experimental temperatures are diverse, which indicates that the temperature has a particular influence on the adsorption characteristics and mechanism of gas on the shale matrix. Therefore, it is necessary to re-explore the applicability of monolayer adsorption (Langmuir model), multilayer adsorption (BET model), and micropore filling ($D$–$A$ model) theories to the adsorption behavior of CH$_4$ and CO$_2$ at different temperatures, respectively. The specifications are as follows:

3.2.1. Fitting Results of the Langmuir Model. The Langmuir model has an excellent degree of fit for CH$_4$ adsorption behavior at different experimental temperatures ($R^2 = 0.9948, 0.9953, 0.9918,$ and 0.98003, respectively). The degree of fit for CO$_2$ adsorption behaviors at different temperatures is significantly distinct ($R^2 = 0.9848, 0.9738, 0.93222,$ and 0.93437, respectively) (Figure 6). For YS-13 and YS-14, the experimental temperatures are higher (100 and 80 °C), and the degree of fit is relatively favorable. Conversely, the degree of fit of YS-15 and YS-16 is relatively lower ($R^2 < 0.94$), indicating that the monolayer adsorption theory is not the most suitable model to describe CO$_2$ adsorption at 30 and 55 °C. The higher the temperature, the better the degree of fit, and the more closely it approaches the monolayer adsorption theory. The reason behind this phenomenon is that the gas diffusion ability in shale becomes more substantial, the adsorption stability becomes worse, and the total adsorption amount becomes smaller with the increase of experimental temperature.\textsuperscript{9,34} In contrast, the adsorption energy between shale matrix and the first layer (monolayer) is higher than that of other adsorption layers (multilayer), results in relatively better adsorption stability at high temperature.

3.2.2. Fitting Results of the BET Model. The degree of fit of the BET model for CH$_4$ is all favorable ($R^2 = 0.9898, 0.9903, 0.9976,$ and 0.9951, respectively) (Figure 7). The degree of fit of YS-15 and YS-16 by using the BET model is higher than that of YS-13 and YS-14, which is contrary to the relevant results of the Langmuir model. Under high temperatures, the velocity and diffusion coefficient of gases are large, and the adsorption behavior of CH$_4$ on shale is closer to that of monolayer adsorption. Therefore, the Langmuir model is more appropriate. Still, at 55 and 30 °C, the adsorption behavior of CH$_4$ on shale is closer to multilayer adsorption of the BET model, with relatively lower molecular velocities and diffusion coefficients. The degree of fit for CO$_2$ adsorption by using the BET model is also excellent ($R^2 = 0.9943, 0.9870, 0.9840,$ and 0.9967, respectively), and the variation of the degree of fit is similar to that of CH$_4$.

3.2.3. Fitting Results of the $D$–$A$ Model. The fitting variable of the $D$–$A$ model is $P/P_0$ in eq 5, while the saturated vapor pressure ($P_0$) changes with a change in the experimental temperature. In this work, the saturated vapor pressure was calculated by using eq 6. It was found that the experimental pressure is higher than the saturated vapor pressure for high-temperature CO$_2$ adsorption experiments, which does not conform to the original theory of the $D$–$A$ model. Therefore, referring to the treatment of Wang et al.,\textsuperscript{35} the physical
meaning of $\rho_g/\rho_a$ is, in essence, synonymous to that of $P/P_0$, and by replacing $P/P_0$, a positive fit can be obtained.

\[
P_0 = P_c \exp \left( \frac{1}{T_c} - \frac{1}{T} \right) \frac{\Delta H}{R} \tag{6}
\]

where $P_c$ is the critical pressure of adsorbed gas, MPa; $T_c$ is the critical temperature of absorbed gas, K; $\Delta H$ is the standard boiling point vaporization enthalpy of adsorbed gas, cal/mol; and $R$ is the general constant of gas, J/mol·K.

The D−A model has the optimum degree of fit of the CH$_4$ adsorption curves, where the $R^2$ values are all greater than 0.99 ($R^2 = 0.9980$, 0.9954, 0.9957, and 0.9914, respectively) (Figure 8). The degree of fit of the CO$_2$ adsorption curves also promises ($R^2 = 0.9939$, 0.9864, 0.9935, 0.9964, respectively) (Figure 8). There is no obvious regularity between the degree of fit vs experimental temperature, which indicates that the D−A model is not only proper for the fitting of CH$_4$ and CO$_2$ adsorption behaviors in shale but also has low sensitivity to temperature and wide application range. The adsorption pattern of CH$_4$ and CO$_2$ is better explained by the micropore filling theory correspondingly.

3.2.4. Applicability of the Adsorption Theories and Models. The degree of fit of the three models to the curves of CH$_4$ absolute adsorption curves is favorable, with the $R^2$ values of all samples are higher than 0.98 (Figure 9). In general, the applicability of D−A > BET > Langmuir. Additionally, the performance of the three models is a discrepancy in the different experimental temperatures. For the Langmuir model, the degree of fit for high-temperature samples is better, which indicates that high-temperature promotes the formation of monolayer adsorption. However, the performance of the BET model is opposite to the Langmuir model, and it is more appropriate for low temperature samples, which indicates that low-temperature promotes the formation of multilayer adsorption. The degree of fit of the D−A model is less affected by temperature and has a high applicability. For CO$_2$ adsorption, the fitting effect of the BET and D−A models (all $R^2$ values are higher than 0.98) is better than that of the Langmuir model in the fitting of CH$_4$ and CO$_2$ adsorption behaviors (Figure 9). The performance of the Langmuir model at high temperature ($R^2 > 0.97$) is apparently more potent than that at low temperature ($R^2 < 0.94$). In contrast, the BET and D−A models do not exhibit apparent regularity for temperature.

With the increase of experimental temperature, the gas diffusion ability increases and the stability of adsorbed gas on the pore surface decreases.$^{5,34,36}$ Therefore, monolayer adsorption is easier to form on the surface of the shale matrix, and high temperature has a particular hindrance to the
The adsorption capacity of CO₂ is evidently stronger than that of CH₄. The discrepancy of molecular structure, molecular size, boiling point, self-diffusion coefficient, and adsorption stability leads to the superiority of CO₂. Therefore, injecting CO₂ into shale reservoirs to enhance gas recovery (CO₂-EGR) is regarded as one of the most potential clean and efficient development schemes. In the 30 and 55 °C curves of Figure 10a, when the experimental pressure is in the range of 10–24 MPa, αCO₂/CH₄ is higher than 10.5. According to the characteristics of the hydrostatic pressure gradient (1 MPa/100 m) and conventional geothermal gradient (2.5–3.0 °C/100 m), the reservoir temperature and pressure conditions of 10 MPa and 30–55 °C can be reached with a burial depth of 1000 m. It is speculated that CO₂ injection can significantly enhance the recovery of CH₄. Furthermore, exploring a deep shale gas reservoir (with a burial depth > 3500 m) has captured attention worldwide. Immature exploited technology and huge development costs limit the commercial development of deep gas reservoirs. The CO₂-EGR process can be regarded as a potential alternative development technology. In Figure 10a, the αCO₂/CH₄ values are lower than 4.5 in 80 and 100 °C. Although it is lower than that of low temperature, the CO₂-EGR process still has considerable application potential.

### 3.4. Implication to the EGR–CCS Process

#### 3.4.1. Implication to the EGR Process

The αCO₂/CH₄ values tend to be stable when reached equilibrium pressure, which indicated that once the underground storage of CO₂ is completed, the possibility of leakage is low. Additionally, in the shale gas reservoirs with a burial depth of over 1000 m, CO₂ behaves like a supercritical fluid and its injection has significant engineering advantages. In a pore system of shale dominated by slit pores, plate-shaped pores, and ink bottle pores, the throat of an ink bottle pore is narrow, and the internal CH₄ molecule is difficult to move out during the process of conventional depressurization and drainage. Wang et al. revealed that supercritical CO₂ would react with organic matter and minerals in the pore wall, which widens the pore throat and increases CH₄ drainage. Additionally, hydraulic fracturing in the shale can be seriously affected by “water sensitivity” and “collapsibility” due to the high clay content of shale, which may cause the internal blocking of pores, damage pore connectivity and influence the effectiveness of hydraulic fracturing. In contrast, fracturing fluid based on supercritical CO₂ has the characteristics of low viscosity, high diffusion, high density, low rock-breaking threshold, and fast speed. Zhang et al. also implied that the injection pressure of the CO₂ fracturing process is lower and the fracture dispersion is wide. Therefore, it is easy for the CO₂ to communicate with the original pore system and form a gas migration network channel.

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**Figure 10.** Variation of αCO₂/CH₄ at different experimental pressures and temperatures. (a) Curves of αCO₂/CH₄ versus experimental pressure and (b) correlation of αCO₂/CH₄ vs experimental temperature.
Although the EGR–CCS process has great application potential, it is not mature yet and several critical bottlenecks exist in the application process. (i) the cost of CO2 acquisition, transportation, and injection is vast, which is regarded as an economic burden at present; (ii) the phase transformation of CO2 is fast and complex, and the change of its properties and state is not completely clear under high pressure and temperature. It is also essential to clarify the reservoir strain caused by the CO2 injection process, as well as the gas migration—displacement—desorption process, to ensure the displacement efficiency and stability of CO2 underground storage; and (iii) the sand carrying capacity of CO2 based fracturing fluid is lower than that of water-based fracturing fluids, and its viscosity is low, which may result in sand plugging the fractures. The above problems are the crucial directions in further work.

4. CONCLUSIONS

(1) The adsorption capacity of CH4 is relatively low at high experimental temperature, and there was no apparent correlation between them; while a linear negative correlation was recorded between CO2 adsorption capacity versus experimental temperature. The D–A model has a perfect degree of fit for CH4 and CO2 adsorption behavior and has a high adaptability to temperature. Micropore filling theory is suitable for simulating gas adsorption behavior in deep and shallow gas reservoirs. The BET model also has a promising degree of fit for CH4 and CO2, while it is more applicable at low temperatures. Contrarily, the degree of fit of the Langmuir model is more suitable for high temperatures. The adsorption behavior of gas in shale tends to transform from monolayer to multilayer with increased temperature.

(2) αCO2/CH4 of the four samples is in the range of 2.64–4.29, 2.47–4.15, 3.72–11.35, and 4.46–12.16, respectively. The values are positively correlated versus experimental pressure and negatively correlated versus experimental temperature. For YS-15 and YS-16, the equilibrium αCO2/CH4 is over 10.5, the injection of CO2 can promote the desorption of CH4. By contrast, the equilibrium αCO2/CH4 of YS-13 and YS-14 is below 4.5, which suggests that the injection of CO2 will enhance CH4 recovery and realize the geological CCS of CO2 with a low leakage risk.

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