

Review Article

Study on Competitive Adsorption and Displacing Properties of CO₂ Enhanced Shale Gas Recovery: Advances and Challenges

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CO₂ enhanced shale gas recovery (CO₂-ESGR) draws worldwide attentions in recent years with having significant environmental benefit of CO₂ geological storage and economic benefit of shale gas production. This paper is aimed at reviewing the state of experiment and model studies on gas adsorption, competitive adsorption of CO₂/CH₄, and displacement of CO₂-CH₄ in shale in the process of CO₂-ESGR and pointing out the related challenges and opportunities. Gas adsorption mechanism in shale, influencing factors (organic matter content, kerogen type, thermal maturity, inorganic compositions, moisture, and micro/nano-scale pore), and adsorption models are described in this work. The competitive adsorption mechanisms are qualitatively ascertained by analysis of unique molecular and supercritical properties of CO₂ and the interaction of CO₂ with shale matrix. Shale matrix shows a stronger affinity with CO₂, and thus, adsorption capacity of CO₂ is larger than that of CH₄ even with the coexistence of CO₂-CH₄ mixture. Displacement experiments of CO₂-CH₄ in shale proved that shale gas recovery is enhanced by the competitive adsorption of CO₂ to CH₄. Although the competitive adsorption mechanism is preliminary revealed, some challenges still exist. Competitive adsorption behavior is not fully understood in the coexistence of CO₂ and CH₄ components, and more experiment and model studies on adsorption of CO₂-CH₄ mixtures need to be conducted under field conditions. Coupling of competitive adsorption with displacing flow is key factor for CO₂-ESGR but not comprehensively studied. More displacement experiments of CO₂-CH₄ in shale are required for revealing the mechanism of flow and transport of gas in CO₂-ESGR.

1. Introduction

Due to increasing combustion of fossil fuels and the ensuing large-scale CO₂ emissions, the high level of CO₂ content in the global atmosphere is believed as the main driving force of global climate change [1, 2], which may cause climate disasters, seriously affecting human life and the earth's ecology [3, 4]. CO₂ capture, utilization, and storage (CCUS) technology is a promising and practical CO₂ mitigation technology by injecting the captured CO₂ into underground formation for permanent sequestration and enhanced oil/gas recovery and other underground energy recovery [5–8], drawing worldwide attentions.

Natural gas is regarded as one of the most promising alternatives of traditional fossil fuels, such as coal and oil,

as it is one of the efficient and clean energy sources for environmental protection. In recent years, large-scale shale gas reservoirs have been discovered worldwide as one of the typical unconventional natural gas resources. The global shale gas is reported as five times conventional gas reserves [9] with the large technically recoverable resources reported in China (1115 tcf), US (665 tcf), and Canada (573 tcf) [10]. The development of shale gas reservoir is imminent. Shale formations are commonly tight with low intrinsic permeability, and thus, it is difficult to be exploited by conventional development technologies. It is necessary to increase permeability and pore connectivity by fracturing technology for exploitation. At present, hydraulic fracturing is the main reservoir reconstruction technology to artificially fracture and extend natural microcracks for shale gas exploitation [6, 7].

However, hydraulic fracturing has many problems such as water consumption, chemical additive pollution, and reservoir damage [11].

Compared to hydraulic fracturing, CO₂ fracturing has many advantages such as reducing fracturing pressure, reducing flow blockage, and avoiding reservoir damage and pollution [6, 12]. The conception of CO₂ enhanced shale gas recovery (CO₂-ESGR) technology comes out by combining CO₂ fracturing and CO₂ injection for shale gas exploitation. CO₂ replaces the adsorbed CH₄ in shale matrix (kerogen or clay) through competitive adsorption and displaces the free CH₄ in the fractured pores during the process of CO₂-ESGR, thereby increasing the recovery of shale gas. Notably, CO₂-ESGR is one of the promising CCUS technologies to store CO₂ into the shale formation for greenhouse gas emission reduction [13]. Thus, CO₂-ESGR has great application potential for both the economic benefit of efficient exploitation of shale gas reservoirs and the simultaneous environmental benefit of CO₂ mitigation.

CO₂-ESGR contains several processes, such as shale fracturing, CO₂ displacement of the free CH₄ in pore and fractures, CH₄ desorption and CO₂ competitive adsorption, and CO₂ geological storage. The schematic diagram of CO₂-ESGR is shown in Figure 1. Therefore, in order to achieve effective development of CO₂-ESGR technology, some relevant key scientific problems must be solved, including mechanism of CH₄ adsorption/desorption, CO₂/CH₄ competitive adsorption mechanism in shale matrix, and CO₂ displacement CH₄ flow and mass transfer mechanism. The adsorption/desorption characteristic of single-component gas (CH₄ or CO₂) in shale has also been fundamentally studied [14–16]. Among these key scientific problems, mechanism of CO₂/CH₄ competitive adsorption in shale matrix and flow and mass transfer in the displacement of CO₂-CH₄ has not been fully understood and has attracted widespread attention and curiosity worldwide. Recently, more and more studies are focused on these issues.

This work is aimed at addressing the issue of CO₂ replacing and displacing shale gas in CO₂-ESGR, link the study on adsorption/desorption of CO₂/CH₄ in shale and flow characteristics of CO₂ displacing CH₄. The advances on competitive adsorption of CO₂/CH₄ during CO₂ displacing CH₄ in shale related to CO₂-ESGR are review, and the challenges and opportunities are address.

2. Gas Adsorption in Shale

The natural gas in shale is generated in situ from the organic-rich deposition through biogenic and thermogenic processes [17]. Shale gas is consisted of predominant CH₄ (>94%), other higher hydrocarbons (ethane, propane, and butane), and minor fraction of inorganic gases [18]. Shale gas is mainly stored in three states: adsorbed gas on the micro/nano-scale pore of shale matrix, free gas in natural cracks and pores, and a small amount of solution gas dissolved in the connate water [19]. The adsorbed CH₄ in the micro/nano-scale pores accounts for a great proportion (20-80%) of the total shale gas resources [14, 20, 21]. Therefore, gas adsorption in shale is one of the most important mechanism

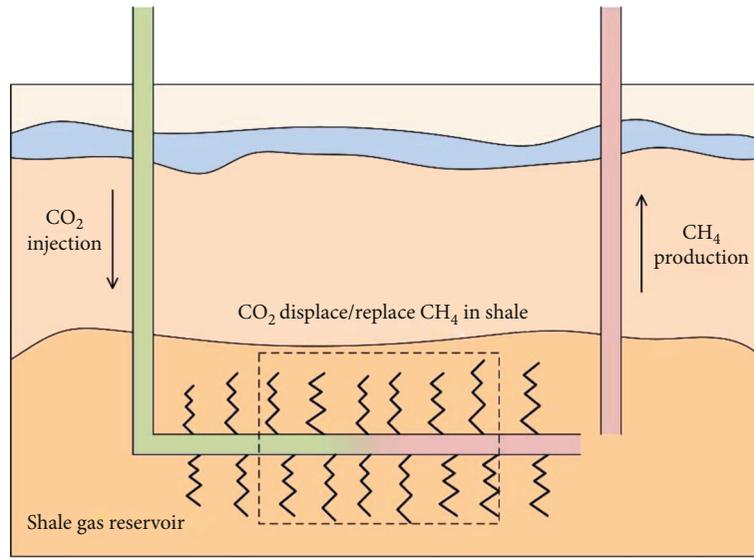
of gas storage. Thus, adsorption/desorption characteristics of CH₄ in shale play a key role in the determination of economic feasibility and exploration mode of shale gas reservoirs. The knowledge of gas storage and transport mechanisms related to adsorption is required for resource quantification and evaluation of long-term production behavior. [22]

2.1. Adsorption Mechanism. Gas adsorption is the accumulation process of gas molecules on the rock surface by two kinds of mechanism: physisorption (physical adsorption) through van der Waals forces and chemisorption (chemical adsorption) through bonds by electron sharing or transfer [23]. Thereby, a high density in adsorbed phase is formed different from the free gas present in the surrounding [24]. Thus, the gas storage potential of shale is increased by twice or more than rocks in absence of adsorption due to the adsorption mechanism [25]. Commonly, the gas adsorption in shale is mainly considered as physisorption [26, 27]. Physisorption is an exothermic process, and the adsorption heat is in the range from 8 to 40 kJ/mol [28]. It is believed that two kinds of physisorption mechanism take place for gas adsorption in shale: monolayer adsorption at low pressures and multilayer adsorption at high pressures [23]. Desorption is regarded as the counter process of adsorption with gas released from shale matrix surface.

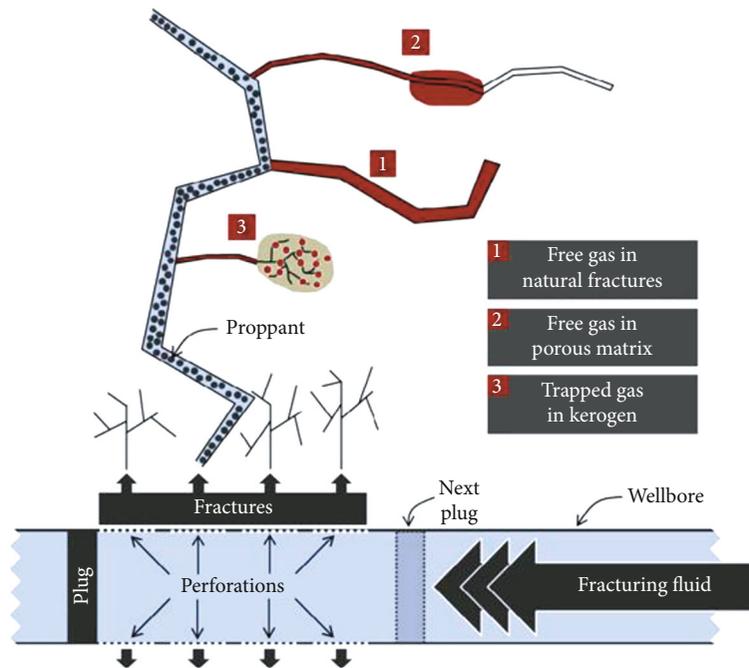
The gas adsorption characteristics in shale are usually evaluated by the measurement of adsorption isotherms in laboratory, which involves measuring the uptake or release of either gas species on a shale sample at certain temperature and pressure conditions [29–32]. Adsorption isotherm curves are commonly measured by gravimetric, volumetric/manometric, and chromatographic methods [30, 33, 34]. Thus, the gas storage capacity in shale due to adsorption can be estimated under certain temperature and pressure according to the adsorption isotherms. Based on the experimental data of adsorption/desorption isotherm, models are established for predicting gas adsorption behavior in shale, such as Langmuir model and Brunauer-Emmett-Teller models.

2.2. Influence of Various Factors on CH₄ Adsorption. Shale commonly consists of organic matter (kerogen), inorganic clay, and other mineral compositions, such as quartz and mica. The related mineral and geological properties of shale play a key role in controlling the gas adsorption characteristics in shale. For the purpose of evaluating shale gas reservoir resources, researchers concentrated on the adsorption/desorption mechanism of CH₄ in shale in the early studies, and the main influencing factors were analyzed: organic matter content, kerogen type, mineralogy, thermal maturity (R_o), moisture, micropore structure and pore size distribution, etc. Thus, the main controlling mechanism of influencing factors is described, and no more details are introduced here because the influence of various factors on adsorption has been reviewed by Rani et al. [24] and Klewiah et al. [32].

The organic matter content in shale is usually quantified by the total organic carbon (TOC), and it is one of the most significant controlling factors on adsorption characteristics. Some studies [22, 35] confirmed that the amount of adsorbed



(a)



(b)

FIGURE 1: (a) Schematic diagram of CO₂ enhanced shale gas recovery; (b) schematic diagram of CO₂ displacing/replacing CH₄ in shale during CO₂ fracturing for enhanced shale gas recovery [12].

CH₄ in shale is proportional to the organic matter content, and the larger TOC can improve the adsorption capacity of CH₄. This phenomenon can take place in almost all kinds of shales. Klewiah et al. [32] summarized a lot of experimental data [22, 29, 35–45] in different shales and confirmed the strong correlation of gas capacity with TOC, shown in Figure 2. The adsorption capacities of CH₄ have strong positive linearity with TOC for both dry and moist shales. The probable reason is that organic richness is believed to be primarily responsible for the microporous nature of shale and the main contributor to the surface area and total pore vol-

ume [43, 46]. Thus, gas adsorption capacity increases with rising content of TOC in shale.

Besides TOC, kerogen type plays a significant role on controlling gas adsorption capacity. Considering the nature of organic matter and surroundings, kerogen is categorized as three types based on its composition and type of generating hydrocarbon [47–49]. Type I, Type II, and Type III kerogen are attributed to extensive aromatization from immature to overmature organic matter [32]. Type I kerogen mainly consists of algal and amorphous kerogen, which is mostly generated from lacustrine and marine environments.

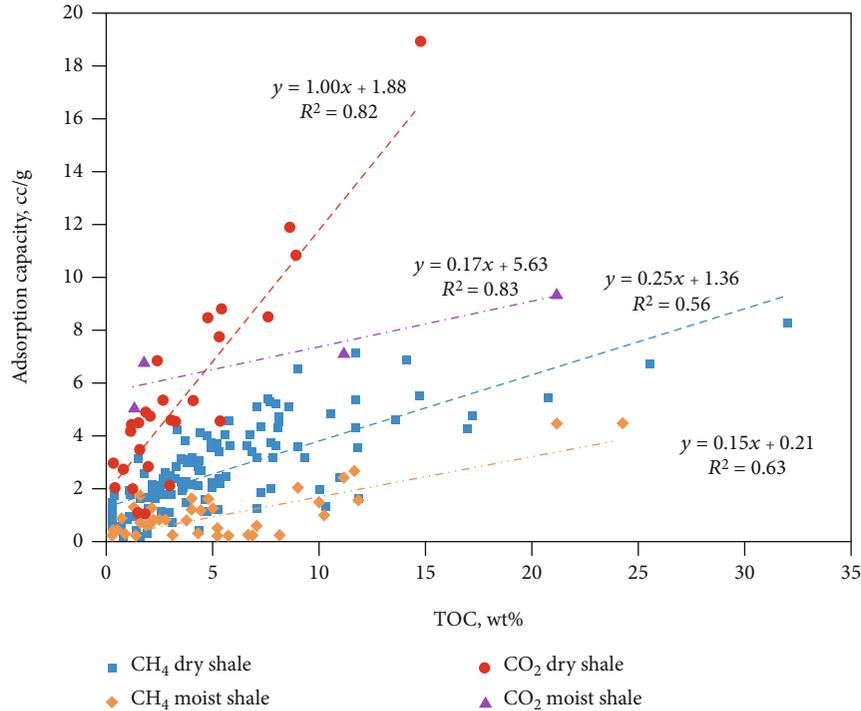


FIGURE 2: Correlation between TOC and CH_4 and CO_2 sorption capacity in dry and moisture shales [32]. Experimental data points are selected from literature [22, 29, 35–45].

Type I kerogen is highly likely to generate oil and has ability to produce gas in the proper thermal maturity. Type II kerogen is rich in hydrogen and low in carbon, and it is formed from mixed terrestrial and marine source materials. Type II kerogen can generate both oil and gas. Type III kerogen is rich in oxygen and poor in hydrogen, and it is formed from terrestrial plant debris. Type III kerogen generally generates gas. Due to the different source rock material and deposition environments of kerogen, some studies [35, 50] have proved that the gas adsorption capacity is in the order of Type III > Type II > Type I.

Thermal maturity (R_o) is another key influencing factor in gas adsorption capacity of shales. Thermal maturity is an indicator to show the heat-driven diagenetic changes of organic matter in sedimentary source rocks to generate hydrocarbons [32]. With the structural transformation of kerogen during maturation, more additional micro/nano-scale pores are generated [50–52]. Correspondingly, the gas adsorption capacity in shale increases with the higher thermal maturity in general, although a few studies found that the thermal maturity has little effect on adsorption [35] or CH_4 adsorption capacity concomitantly decrease with increasing maturity [50, 53].

The main inorganic compositions of shale include clay, quartz, mica, albite, pyrite, carbonate, and mineral, and these inorganic compositions, particularly the clay minerals, contribute enormously to the inner surface area and micropore volume and affect adsorption properties [54–56]. Thus, clay types (illite, smectite, kaolinite) and contents are one of the significant factors on gas adsorption in shale. The larger clay contents in shale are believed to increase the gas adsorption

capacity [22, 57, 58]. However, the influence of inorganic mineral matters on different gas adsorption shows different behaviors in various studies. CH_4 adsorption capacity is affected little by the inorganic matter in some studies [59], but several researches also show that the inorganic matter has significant influence on CO_2 adsorption [29]. Nevertheless, more researchers have proven that the mineral components have appreciable sorption capacity for both CH_4 and CO_2 [22, 40].

Moisture also plays a crucial role on analysis of gas adsorption characteristics. The effect of moisture in shale is always related to organic matters and clay contents [53, 60]. It is reported that water molecules would compete with gas for identical adsorption sites on organic matters via hydrogen bonding [22, 35, 45, 50] and interact with preadsorbed water and charged surfaces of mineral matter (especially chemisorptive clay) [32]. Thus, moisture weakens the adsorption capacity of CH_4 in shale, shown in Figure 2.

TOC content and shale mineral composition analysis may not fully explain the gas adsorption mechanism in shale; pore volume (especially micro/nano-scale pores) and inner surface area are crucial on the gas adsorption [61]. Rexer et al. [61] showed that the main controlling factor for the amount of adsorbed gas in shale is the volume of adsorption pores, and most of the adsorbed CH_4 is in microscale pores with a diameter of less than 6 nm. Xue et al. [62] conducted on visualization study of shale micropore structure and mineral composition analysis and their influence on adsorption and found that the gas adsorption capacity is linearly related to the product of TOC and surface porosity.

2.3. Adsorption Difference between CO_2 and CH_4 in Shale. Due to the physical properties difference, CO_2 and CH_4 have significantly different adsorption behavior in shale. The typical adsorption isotherms for CH_4 and CO_2 have been studied by Weniger et al. [29], shown in Figure 3. Under different TOC condition, the excess adsorption of CH_4 in shale consistently increases with pressure and gradually reach a constant value at high pressures [32, 63–65]. The adsorption of CO_2 is closely related to the phase state: in gas state, the excess adsorption of CO_2 increases with pressure by having a larger increasing rate than CH_4 before supercritical point, then reaches the maximum in the vicinity of supercritical pressure and then decreases in supercritical state. The mentioned difference in adsorption characteristics between CO_2 and CH_4 has also been clearly reported in other experiments [45, 66–70].

Compared to CH_4 adsorption in shale, some influencing factors have different performance for CO_2 adsorption in shale, which will be described as follows. Similar with CH_4 , CO_2 adsorption capacity increases with higher TOC, shown in Figure 3. More precisely, the adsorption capacities of both two gases have strong positive linearity with TOC, summarized by Klewiah et al. [32], illustrated in Figure 2. Generally, the adsorption capacity of CO_2 is much larger than that of CH_4 at the same TOC for both dry and moist shale, and the increasing rate of the former versus TOC is much higher than that of the latter in dry shale. In contrast to that, the adsorption capacity of CH_4 in the moist shale is lower than that in dry one; CO_2 adsorption capacity in moist shale may larger than that in dry one at low TOC, shown in Figure 2. Results of experiments and molecule grand canonical Monte Carlo (GCMC) simulations in Huang et al. [70] showed that the maximum adsorption capacity of gas molecules for both CO_2 and CH_4 on kerogen is proportional to the effective pore volumes, which increases with kerogen maturity but decreases with moisture content. The effect of other factors on adsorption, such as thermal maturity and inorganic components, shows similar for both CO_2 and CH_4 , which was described by Isaac et al. [32]

2.4. Adsorption Models. Adsorption models, such as Langmuir model and Brunauer-Emmett-Teller models, are frequently built based on the experimental adsorption isotherms. For the main adsorption mechanism of CH_4 in shale, Langmuir model is built for the evaluation of monolayer adsorption behavior, and Brunauer-Emmett-Teller (BET) and Freundlich's isotherms are established for the multilayer adsorption (Table 1) [23].

Langmuir model and its improved model [15, 35, 61] are widely used for the adsorption/desorption of single-component gas under the conditions of low pressure in shale. Lu et al. [30] proved that the Langmuir model can accurately predict the adsorption characteristics at a single temperature, but the adsorption prediction of Langmuir under multitemperature conditions is not so accurate, while the bi-Langmuir model has a better prediction accuracy on the adsorption characteristics of single-component gas in shale by considering the influence of temperature changes.

Most of shale gas reservoirs are usually located in depth of 2000–4000 m underground, and the reservoir temperatures are in the range of 96–122°C with the pore pressures of 15–25 MPa [69]. The critical conditions are 31.1°C and 7.4 MPa for CO_2 and -82.6°C and 4.6 MPa for CH_4 [74, 75], and thereby, CH_4 and CO_2 are both in supercritical state in shale reservoirs. As the conventional adsorption model, such as Langmuir model, cannot precisely predict the adsorption behavior under shale gas reservoir conditions of high temperature and high pressure, and more fine models are needed in response to this situation.

The supercritical adsorption models based on adsorption potential theory, such as supercritical Dubinin-Radushkevich (SDR) model, are developed for accurate description of gas adsorption behaviors in shale under high-temperature and high-pressure reservoir conditions. However, Tian et al. [76] found that there is no significant improvement for SDR model in prediction of the maximum absolute CH_4 adsorption in the Sichuan Basin shale by comparing to Langmuir model. Song et al. [77] proposed an adaptive L-SDR model based on the combination of SDR model and Langmuir model, and the comparison of the adaptive L-SDR, Langmuir, and SDR for prediction of gas adsorption isotherm in Tarim Basin shale showed that the L-SDR model more accurately predicts the adsorption characteristics of supercritical CH_4 in shale at both low and high temperatures. The lattice density functional theory (LDFT) model is another supercritical adsorption model to predict the adsorption enthalpy. Hwang et al. [78] showed that even under high pressure, the predictive ability of the LDFT model was proved in revealing the pore-dependent adsorption behavior. Considering the difference in the adsorption mechanism of CH_4 with different pore diameters, Zhou et al. [79] proved that the adsorption form of CH_4 in shale is not only through single micropores or single layer adsorption and established a new supercritical adsorption model for shale gas. This supercritical adsorption model presents the adsorption mechanism in micro/nano-scale pores by comprehensively combining the coexistence of pore filling and single-molecule adsorption.

3. Competitive Adsorption between CH_4 and CO_2

The conception of CO_2 -ESGR for shale gas exploitation has a unique promising potential through CO_2 competitive adsorption to release the adsorbed CH_4 from shale matrix into the fractures and cracks for production and thus to increase shale gas recovery [32]. Thus, the competitive adsorption of CO_2 to CH_4 in shale plays the key role on CO_2 -ESGR. When CO_2 injected into shale reservoir, CO_2 will compete the adsorption sites on the inner surface of shale matrix with CH_4 . Then, the desorption of CH_4 and adsorption of CO_2 synchronize in the shale formation due to competitive adsorption, and the flow and mass transfer in this process are schematically shown in Figure 4.

3.1. Experimental Study on CO_2/CH_4 Competitive Adsorption. The competitive adsorption characteristics of

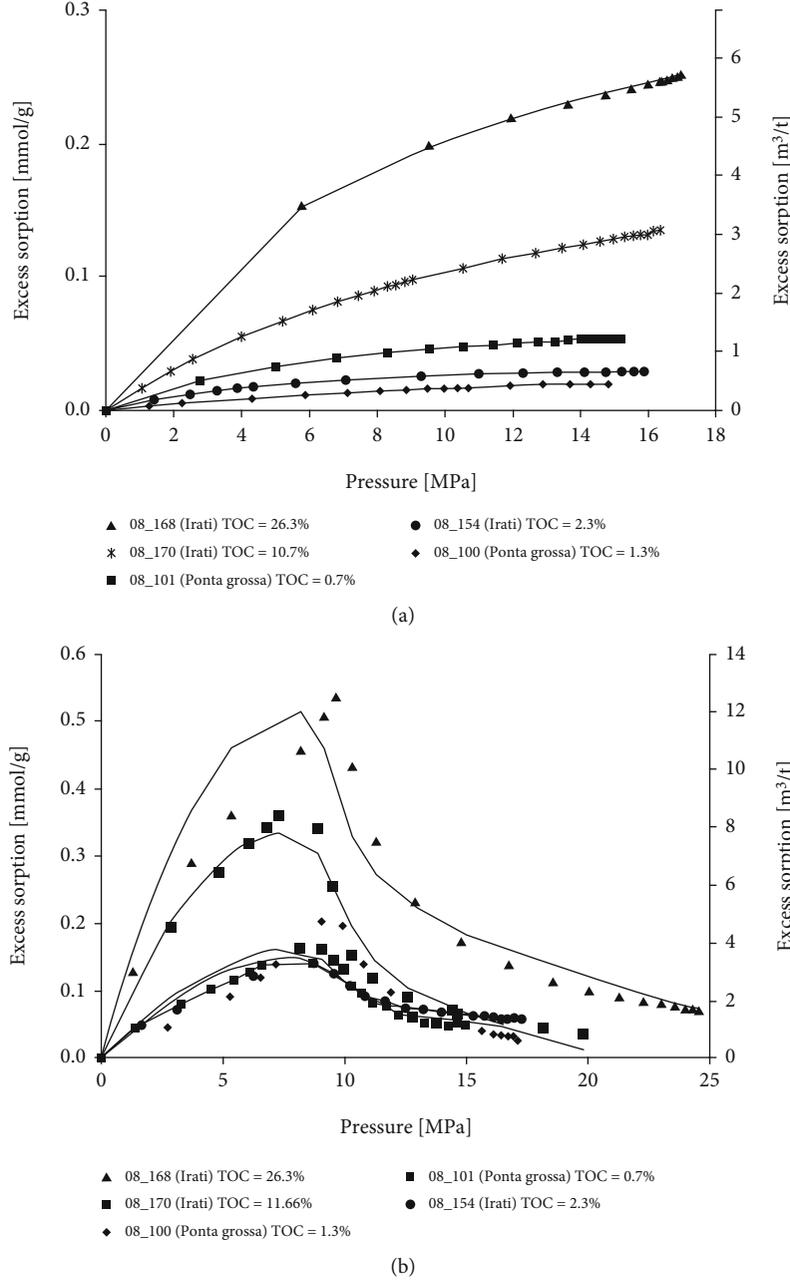


FIGURE 3: Adsorption isotherm (excess sorption vs. pressure) for (a) CH_4 and (b) CO_2 on crushed dry shale samples of the Parana Basin in Brazil at a temperature of 45°C [29].

TABLE 1: Typical models for monolayer and multilayer adsorption.

Model	Formula	Reference
Langmuir	$q = Q_l k_l p / (1 + k_l p)$	[71]
BET	$q = Q_m k_b p / (p_s - p) [1 + (k_b - 1)(p/p_s)]$	[72]
Freundlich	$q = k_f p^n$	[73]

where q is the gas adsorption, mg/g; p is the pressure, bar; Q_l is the Langmuir maximum adsorption, mg/g; k_l is the Langmuir constant; p_s is the saturation pressure, bar; k_b is the constants of BET isotherm; Q_m is the maximum uptake, mg/g; and k_f and n are the constants of Freundlich isotherm.

CO_2 to CH_4 were initially investigated by comparative analysis of the adsorption behavior between single-component gas of CO_2 and CH_4 . Nuttall et al. [44] first observed that the adsorption capacity of pure CO_2 is approximately 5 times greater than that of CH_4 in Devonian black shales at the same conditions. The adsorption capacity of pure CO_2 was also reported consistently higher than that of CH_4 in various kinds of shale by many following research [16, 26, 29, 40, 41, 80–84]. Klewiah et al. [32] summarized some related adsorption experiments of single-component gas of CO_2 and CH_4 , reported the CO_2/CH_4 adsorption ratio in the range of 1.3–10 for dry shale, and revealed moisture weakening the CO_2/CH_4 adsorption ratio. Similar to CH_4 , the

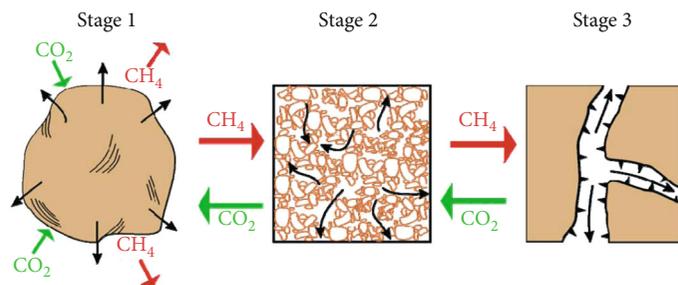


FIGURE 4: Schematic diagram of the competitive adsorption and transport of CO_2 and CH_4 in shales [13].

increase in pressure and organic carbon content contributes to adsorption capacity of CO_2 in shale, while the temperature is the opposite. Compared to CH_4 , the desorption process of CO_2 has an obvious hysteresis effect, which is conducive to long-term CO_2 storage [83, 85]. The moisture, matrix expansion, and pore throat size may affect the hysteresis of CO_2 desorption behavior, but the mechanism of CO_2 desorption hysteresis has not been thoroughly revealed [86, 87].

The adsorption experiments of CO_2 - CH_4 mixture system [42, 88–92] show that the greater adsorption affinity exists for CO_2 in shales than CH_4 even though sometimes CH_4 is preferentially adsorbed in the adsorption experiment of CO_2 - CH_4 mixture. It is revealed that CO_2 has a higher adsorption capacity in the coexistence of CO_2 and CH_4 , proving that competitive adsorption is beneficial to the implementation of CO_2 -ESGR. However, Qi et al. [91] confirmed that the adsorption characteristics are not only related to adsorption affinity but also affected by the partial pressure of the components in the mixture system, and the competitive adsorption ratio of CO_2/CH_4 in the mixture system may be smaller than that under condition of single-component adsorption. Thus, more experiments of CO_2 - CH_4 mixture adsorption/desorption are needed for competitive adsorption characteristics and mechanism.

Except the competitive adsorption of static gas adsorption experiments of single-component gas and CO_2 - CH_4 mixture system, several researchers carried out dynamic competitive adsorption experiment on CO_2 - CH_4 exchange characteristics [93–95]. The competitive adsorption ratio and enhanced recovery of shale gas by injection of CO_2 were also proved by these dynamic experiments.

3.2. Mechanism of CO_2/CH_4 Competitive Adsorption. As for the mechanism of competitive adsorption between CO_2 and CH_4 in shale, the competition for adsorption sites plays a key role on CO_2 replacing CH_4 . Specifically, molecular size of gas, interaction energy (thermodynamic forces) between gas and shale matrix, and accessibility of gas into the shale microporous network (steric forces) are considered as the important controlling factors of competitive adsorption between CO_2 and CH_4 [32]. The molecular characteristic difference between CO_2 and CH_4 is crucial: CH_4 molecule is tetrahedral geometry with a relative larger kinetic diameter of 3.80 \AA , and CO_2 molecule is linear molecular with a smaller kinetic diameter of 3.30 \AA [26, 74, 75, 96], shown in Table 2. Due to the smaller molecular size, CO_2 can easily access into

micro/nano-scale pores with smaller diameter which may be difficult for CH_4 , and thus, CO_2 is favourable to contact larger surface and adsorption sites in shale matrix [32, 97]. Moreover, CO_2 can interact more strongly with functional groups in kerogen because of higher quadrupole moment, and thus, CO_2 is more prone to physical adsorption caused by van der Waals force than CH_4 [26, 98, 99]. Zhao and Wang [95] revealed that the surface of shale organic matter has a stronger affinity for CO_2 than CH_4 , and then, CO_2 competes for adsorption sites to replace the adsorbed CH_4 on the surface of the matrix. The higher critical temperature of CO_2 also favour the competitive adsorption to replace CH_4 [97]. As an endothermic reaction, desorption process of CH_4 needs a relative lower of the adsorption heat than that of CO_2 , and thus, desorption of CH_4 from shale can be more easily realized in the coexisting CO_2 adsorption process. The unique supercritical properties of CO_2 , such as liquid-like density, gas-like diffusion, gas-like viscosity, and wetting to shale surface, facilitate the effective contact with shale surface and adsorption sites and thus improve competitive adsorption to CH_4 [32, 100].

Molecular simulation is a good method to investigate adsorption mechanisms from the view of molecular motion and reaction. Recently, some grand canonical Monte Carlo (GCMC) simulations [20, 70, 101–103], one typical molecular simulation method for adsorption, were conducted to explore the mechanism of CO_2/CH_4 competitive adsorption. Huang et al. [20, 70] studied the competitive adsorption behavior of CO_2/CH_4 in dry and moist realistic kerogen models of different organic types. The simulation results showed that the CO_2/CH_4 adsorption selectivity increases with increasing CO_2 concentration at low pressure for kerogen models of higher maturity but decreases with CO_2 mole fraction for lower mature kerogen models. Specifically, CO_2/CH_4 adsorption selectivity increases with the enterable pore volume fraction in the immature organic type. The CO_2/CH_4 adsorption selectivity decreases first and then increases with the moisture content while the adsorption of CO_2 is more sensitive with moisture than that of CH_4 . However, moisture can potentially boost the displacement of CH_4 by CO_2 at certain conditions. Zhou et al. [101–103] also conducted a series of molecular simulations on CO_2 and CH_4 adsorption for enhanced shale gas recovery and explore the effect of moisture and brine (salinity). Zhou et al. [102] explored the shale gas recovery mechanisms of CO_2 injection in kerogen slit pores and analyzed the effect of moisture. CH_4

TABLE 2: Physical properties and molecular parameters of CO₂ and CH₄ [104].

Property	CO ₂	CH ₄	Reference
Molecular mass, m (g/mol)	44	16	—
Critical temperature, T_c (K)	304.2	190.5	[74, 75]
Critical pressure, P_c (MPa)	7.4	4.6	[74, 75]
Critical density, ρ_c (kg/m ³)	467.6	162.7	[105]
Adsorbed phase density, ρ_a (kg/m ³)	1028	372	[74, 75]
Molar polarizability, αM (cm ³ /mol)	7.34	6.54	[106, 107]
Kinetic diameter, σ_k (Å°)	3.30	3.80	[74, 75, 96]
Collision diameter, σ_{col} (Å°)	4.00	3.82	[96]
Effective molecule diameter, $\sigma_{eff} = \sqrt{\sigma_k \cdot \sigma_{col}}$ (Å°)	3.63	3.81	[96]

adsorption capacity in the CO₂-CH₄ mixture decreases with increasing moisture due to the accumulated H₂O clusters impeding the pore filling of CH₄ in the kerogen slit pores. Compared to pressure drawdown, CO₂ injection can release CH₄ molecules in the adsorption layer; the CH₄ recovery ratio of CO₂ injection increases with the increasing moisture. Zhou et al. [103] found that the total uptake of CH₄ and CO₂, including adsorption in kerogen surfaces and dissolution at kerogen/water interface and in water/brine, decreases linearly with increasing salinity. Salinity effects on CO₂ uptake are proved as complicated. The CO₂ adsorption decreases due to the pore volume in kerogen surfaces occupied by brine, but the remarkable enhancement in CO₂ solubility in brine is observed. Moreover, the wettability of kerogen surface is transformed from a partially water-wetting into a less water-wetting interface caused by the existence of CO₂ adsorption, though this effect is inhibited by salinity.

The competitive adsorption mechanism is fundamentally revealed, but how to accurately quantify the competitive adsorption and evaluate the adsorption ratio of CO₂/CH₄ is not very clear, especially under the condition of mixture. More related experiments and models study should be conducted.

4. Displacement of CH₄ by CO₂ in Shale

4.1. Flow Mechanism in Shale. CH₄/CO₂ adsorption and desorption in shale are coupled with multiscale and multi-field flow from shale matrix and fracture network to wellbore in the process of CO₂-ESGR [97]. Therefore, the flow and mass transfer process is very complicated and involves different mechanisms. The flow and transport mechanisms in different scales related to CO₂-ESGR are shown in Figure 5 [52].

On the microscopic mechanism, the main interaction of gas flows in porous media is the collisions between gas molecules and the collisions between gas molecules and the walls of pores [108]. Thus, the mean free path of gas molecules and pore scales plays key roles on determination of flow regime in porous media. Knudsen number, K_n , is proposed to differentiate the flow regime in tight porous media. Knudsen number is defined as, $K_n = \bar{\lambda}/r_{pore}$, where $\bar{\lambda}$ is the mean free path of gas molecules and r_{pore} is the radius of pore in porous media. With the increase of Knudsen number, the collision probab-

ility between gas molecules decreases while the collision probability between gas molecules and the pore wall increases. Correspondingly, the flow in micropores is divided into [109] continuum flow (Darcy flow), slip flow, transition flow, and free molecular flow. Simultaneously, the microscopic mass transfer mechanism of shale gas is the viscous flow, Knudsen diffusion, free molecular diffusion (Fick diffusion), and surface diffusion [110]. The relationship between Knudsen number and gas flow regime under different pore scales and the corresponding governing equation are shown in Table 3.

For single-component gas flow, Javadpour et al. [114, 115] analyzed the gas flow in shale and micropore structure characteristics of shale and believed that non-Darcy flow occurs in the micropores. The flow regime of this kind of non-Darcy flow should be determined based on the mean free path of gas molecules and Knudsen number. Freeman et al. [116] further pointed out that non-Darcy flow will occur when the pore throat diameter of shale is equivalent to the molecular mean free path length. At this time, there is a strong correlation between permeability and pore pressure. The gas flow is Darcy flow in natural cracks and artificial fractures while it is non-Darcy flow in the shale matrix [117]. Li et al. [118] believed that the gas flow in micropore throats is slip flow and transition flow, and the mass transfer mechanism is mainly the combination of viscous flow and Knudsen diffusion at the temperature of 300-360 K and pressure of 1-100 MPa in shale reservoirs. Knudsen diffusion is negligible, and viscous flow is dominant in cracks larger than 100 nm, which is applicable to Darcy's law. In shale pores or fractures with a diameter less than 10 nm, molecular free flow comes into play, and surface diffusion is small [119]. Sun et al. [119] further explored the effects of the adsorption/desorption of CH₄ in kerogen organic matter, the pore volume occupied by the adsorption layer, and the surface diffusion of the adsorption layer on the gas flow and mass transfer. Song et al. [120] combined non-Darcy flow (including Knudsen diffusion, gas adsorption, and surface diffusion) with the influence of critical pore space under real gas temperature and pressure conditions to study the gas migration mechanism.

4.2. Displacement Experiments of CO₂-CH₄. As for the process of CO₂ displacing CH₄ in shale, the gas flow and mass

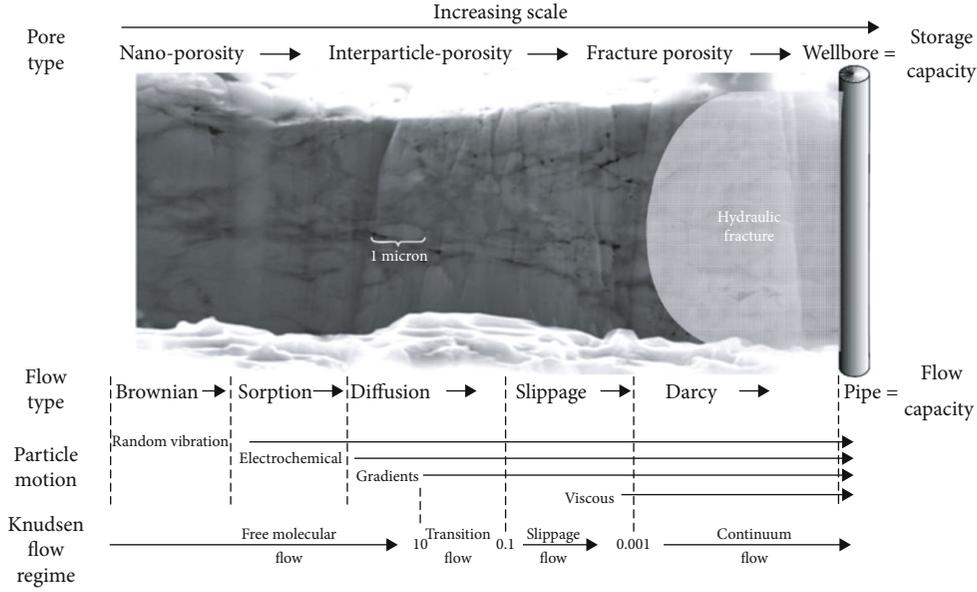


FIGURE 5: Multiscale migration mechanism of gas in shale [52].

TABLE 3: Characteristics of various flow regime under different Knudsen number [111].

Flow regime	K_n range ^{a,b}	Models	Comments
Continuum flow	$K_n < 0.01$	Darcy's equation for laminar flow and Forchheimer's equation for turbulent flow	Assumes immobile fluid at the pore wall, and no permeability correction is generally required.
Slip flow	$0.01 < K_n < 0.1$	Darcy's equation with Klinkenberg's correction or Knudsen's correction	Klinkenberg's correction is generally implemented due to its easiness, and Knudsen's correction is more accurate.
Transition flow	$0.1 < K_n < 10$	Darcy's law with Knudsen's correction can be applied. Alternative method is Burnett's equation with slip boundary condition ^c	Knudsen's diffusion equation is a more reliable approach, especially when K_n is closer to 10.
Free molecular flow	$K_n > 10$	Knudsen's diffusion equation ^d , alternative methods are DSMC and lattice Boltzmann ^c	Usually occurs in shale formations where the pore throat radius is very small.

^aThis Knudsen number classification is taken from Karniadakis et al. [112]. ^bSome reference suggests ($K_n < 0.001$) as a cut off for continuum flow [109]. ^cFor more details, see Agarwal et al. [113]. ^dKnudsen's diffusion can coexist with bulk and surface diffusion.

transfer are more complicated than single-component gas flow. Different from CH_4 flow in shale, the competitive adsorption of CO_2/CH_4 and convective dispersion occur in the miscible displacement in the fracture-matrix dual media of fractured shales. The mass transfer characteristics of miscible displacement of $\text{CO}_2\text{-CH}_4$ in porous media under multifield coupling play the crucial role in $\text{CO}_2\text{-ESGR}$. As an important physical property describing the degree of mixing of two phases in the porous media, the dispersion characteristics in the displacement of $\text{CO}_2\text{-CH}_4$ are one of the convective mass transfer characteristics that researchers focus on.

The early studies on the displacement properties and dispersion characteristics of $\text{CO}_2\text{-CH}_4$ in porous media were mainly carried out for the CO_2 enhanced gas recovery ($\text{CO}_2\text{-EGR}$) in conventional natural gas reservoirs. Mamora and Seo [121] and Liu et al. [122] verified the technical feasibility of $\text{CO}_2\text{-EGR}$ by visualization CT experiments of $\text{CO}_2\text{-CH}_4$ displacement. Honari et al. [123] and Zhang et al.

[124] proposed that residual water would delay the flow migration by blocking the pore pathway, causing the tailing of CO_2 breakthrough curve and non-Fick phenomenon in $\text{CO}_2\text{-CH}_4$ displacement. However, the seepage mass transfer mechanism in the conventional natural gas reservoirs is different from that in shale reservoir due to the higher porosity and permeability.

Compared to the conventional natural gas reservoirs, the seepage mass transfer characteristics in coalbed methane reservoirs are closer to that in shale reservoirs due to their similar geological attributes. Aiming at CO_2 enhanced coalbed methane recovery ($\text{CO}_2\text{-ECBM}$), Shi et al. [125] combined the extended Langmuir model and Fick's law to explore the displacement properties of $\text{CO}_2\text{-CH}_4$ in the coal and analyzed the dynamic competitive desorption characteristics. Some studies also confirmed that the replacing efficiency of CH_4 was enhanced by CO_2 due to competitive adsorption effect with comparing N_2 displacement experiments [126,

127]. It is also verified in the displacement experiments that the moisture can prevent the CO_2 binding to adsorption sites and then affecting the displacement efficiency [128].

There are relatively few studies on the displacement study of CO_2 - CH_4 and the dynamic competitive adsorption in shale related to CO_2 -ESGR. Du et al. [129–131] conducted a series of CO_2 - CH_4 displacement experiments in the crushed shale pack for the displacement properties and dispersion characteristics. Du et al. [129] first analyzed the CH_4 recovery efficiency and CO_2 storage efficiency in displacement experiments. The experimental results showed that CO_2 has a larger dynamic adsorption rate and adsorption capacity, which ensures the feasibility of CO_2 -ESGR. It is also found that the competitive adsorption between CO_2 and CH_4 will cause fluctuations in pore pressure, which in turn will enhance dispersion and produce a wider range of CO_2 - CH_4 mixed phase regions. Du et al. [130] further explored the influence of CO_2 injection pressure on the dispersion characteristics in CO_2 - CH_4 displacement experiment. Based on the convective dispersion theory, it is found that CO_2 diffusion is dominant under the condition of lower CO_2 injection pressure, and the mass transfer coefficient and the miscible area increase with the increasing injection pressure, while the competitive adsorption between CO_2 and CH_4 is becoming obvious. The comparison of CO_2 , N_2 , and CO_2/N_2 mixtures was also conducted; a higher CH_4 recovery existed in CO_2 displacement than that in N_2 displacement [131]. The displacement efficient of CH_4 by CO_2 was also compared with N_2 in simulation, and it is verified that competitive adsorption leads to a larger recovery for CO_2 displacing shale gas [132].

5. Challenges and Opportunities

The adsorption/desorption of shale gas, competitive adsorption of CO_2 to CH_4 , and flow mechanism play the key role on shale gas reservoir exploitation. To our knowledge, some challenges and opportunities on these research topics are arising in the process of CO_2 -ESGR.

A lot of experimental and modelling studies on adsorption/desorption have been conducted in crushed shale samples, especially for CH_4 , and the adsorption mechanism of CH_4 is fundamentally revealed. Due to some shale reservoirs are in deep formation, it is necessary to ascertain the gas adsorption mechanism under high temperature and high pressure. However, the gas adsorption experiments in intact shale cores under field condition are still scarce, and more relevant adsorption studies need to be carried out. Correspondingly, accurate supercritical adsorption models also need to be developed for enriching the comprehensive knowledge of gas adsorption mechanism in shale. Compared to CH_4 , CO_2 has different physical properties and different adsorption behaviors, especially in the supercritical. The adsorption mechanism of CO_2 is not fully revealed, especially under supercritical state, and thus, more experiments and models research on CO_2 adsorption/desorption are urgently needed.

The competitive adsorption of CO_2 to CH_4 is basically proved by a lot of comparative adsorption experiments of pure gas composition and some adsorption studies of CO_2 -

CH_4 mixtures in shale. However, the competitive adsorption has different behavior in the adsorption experiments of single-component gas and CO_2 - CH_4 mixture system. To quantitatively evaluate the competitive adsorption, adsorption ratio of CO_2/CH_4 also shows different for the experiment of single-component gas and mixtures. The CO_2 - CH_4 mixture adsorption is more close to realistic situation, but the related mixture adsorption experiments are in scarcity, especially under the field conditions. Notably, more dynamic competitive adsorption experiments are not adequate for revealing the dynamic exchange mechanism of CO_2 - CH_4 . Considering the different properties between CO_2 and CH_4 , the competitive adsorption mechanism is qualitatively analyzed. However, how to accurately predict the adsorption CO_2 or CH_4 component in CO_2 - CH_4 mixture system and quantify the competitive adsorption are still the important unsolved problems. Maybe, the future work should pay attention on establishment of quantification model on competitive adsorption of CO_2 to CH_4 in shale.

The knowledge of flow mechanism in on certain flow regime has been relatively well developed and understood. The shale gas flows through pathway in different sizes of microscale/nano-scale pores and fractures in shale during the exploitation of shale gas reservoir. Thus, different flow regime is coexisted on this condition. The coupling of flow in different flow regime is one of the key controlling factors for accurately predicting shale gas transport, which has not been fully understood and needs thorough study. Concerning CO_2 -ESGR, the injection of CO_2 makes the flow and gas transport more complicated. The mechanism of competitive adsorption of CO_2 to CH_4 coupled with flow and CO_2 - CH_4 dispersion is not fully ascertained. CO_2 - CH_4 dynamic displacement studies are scarce for comprehensive analysis of the coupling of competitive adsorption with various gas flow regime. In the opinion of this work, future studies may should concern the dynamic competitive coupling with different flow regime in aspects of experiments and models in the miscible displacement of CO_2 - CH_4 for CO_2 -ESGR.

6. Conclusions

Due to both the environmental effect of CO_2 geological storage and economic effect of shale gas exploitation, CO_2 enhanced shale gas recovery (CO_2 -ESGR) draws worldwide concerns in recent years. This work summarizes the existing knowledge on the mechanism of single-component gas adsorption, competitive adsorption, and displacement of CO_2 - CH_4 in shale related to CO_2 -ESGR. The advances of experimental and model studies on these research topics are reviewed. Some conclusions are drawn as follows:

- (i) As unconventional gas resources, shale gas is an important clean fuel with large reserves worldwide. CO_2 enhanced shale gas recovery has great potential to exploit shale gas reservoirs with permanently storing CO_2 into underground formation
- (ii) Generally, gas adsorption in shale is two types of physical adsorption: monolayer adsorption at low

pressure and multilayer adsorption at high pressure. Gas adsorption capacity shows positive relationship with TOC, thermal maturity, and clay content of shale and negative with moisture

- (iii) Adsorption capacity of CO₂ in shale is much larger than that of CH₄ even with the coexistence of CO₂-CH₄ mixture. Due to the unique properties of CO₂, shale matrix shows a stronger affinity with CO₂, and CO₂ can be more easily adsorbed on the inner surface of shale matrix than CH₄
- (iv) Four types of flow regime exist in the gas flow related to shale gas exploitation. Generally, it is Darcy flow for shale gas flow in natural cracks and artificial fractures larger than 100 nm, slip flow and transition flow for gas flow in shale micropore throats in 10~100 nm, and free molecular flow for gas flow in micro/nano-scale pores and cracks
- (v) Compared to single-component gas flow in shale, displacement flow of CO₂-CH₄ is very complicated with mass transfer between two gases. Dynamic studies on displacement of CO₂-CH₄ in shale prove that CH₄ recovery is significantly enhanced due to the competitive adsorption
- (vi) To our knowledge, some challenges and opportunities in these research topics are also proposed
- (vii) More experiment adsorption study in intact shale cores under field condition for supercritical CH₄ and CO₂ is scarce, and the corresponding accurate supercritical adsorption model is urgently needed for revealing gas adsorption mechanism in shale
- (viii) To ascertain competitive adsorption mechanism, more CO₂-CH₄ adsorption experiments under field conditions, especially dynamic experiments, should be conducted to determine the CO₂/CH₄ adsorption ratio. Corresponding, establishment of quantification model on competitive adsorption of CO₂ to CH₄ in shale should draw attentions in the future work
- (ix) Dynamic competitive adsorption coupling with flow in the displacement of CO₂-CH₄ plays the key role on CO₂-ESGR but is not fully understood. The future work should look into the coupling of various flow regime, competitive adsorption of CO₂-CH₄, convection dispersion, etc

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

- [1] WMO, "WMO greenhouse gas bulletin: the state of greenhouse gases in the atmosphere based on global observations through 2018/2019."
- [2] S. Liu, C. Ji, C. Wang et al., "Climatic role of terrestrial ecosystem under elevated CO₂: a bottom-up greenhouse gases budget," *Ecology Letters*, vol. 21, no. 7, pp. 1108–1118, 2018.
- [3] H. Coninck, M. Loos, B. Metz, O. Davidson, and L. Meyer, "IPCC special report on CO₂ capture and storage," IPCC, Montreal, 2005.
- [4] IPCC, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, T. F. Stocker, D. Qin, G. K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley, Eds., Cambridge University Press, Cambridge, UK, 2013.
- [5] A. Najafi-Marghmaleki, A. Barati-Harooni, and A. H. Mohammadi, "Impact of gas impurities on CO₂ mole fraction: application in carbon capture and storage (CCS) processes," *International Journal of Greenhouse Gas Control*, vol. 57, pp. 173–184, 2017.
- [6] H. Xie, X. Li, Z. Fang et al., "Carbon geological utilization and storage in China: current status and perspectives," *Acta Geotechnica*, vol. 9, no. 1, pp. 7–27, 2014.
- [7] A. Rogala, K. Ksiezniak, J. Krzysiek, and J. Hupka, "Carbon dioxide sequestration during shale gas recovery," *Physicochemical Problems of Mineral Processing*, vol. 50, no. 2, pp. 681–692, 2014.
- [8] S. Liu, R. Agarwal, B. Sun et al., "Numerical simulation and optimization of injection rates and wells placement for carbon dioxide enhanced gas recovery using a genetic algorithm," *Journal of Cleaner Production*, vol. 280, article 124512, 2021.
- [9] R. D. Vidic, S. L. Brantley, J. M. Vandenbossche, D. Yoxtheimer, and J. D. Abad, "Impact of shale gas development on regional water quality," *Science*, vol. 340, no. 6134, 2013.
- [10] EIA, *Technically recoverable shale oil and shale gas resources: an assessment of 137 shale formations in 41 countries outside the United States*, U.S. Energy Information Administration, 2013.
- [11] H. Yin, J. Zhou, Y. Jiang, X. Xian, and Q. Liu, "Physical and structural changes in shale associated with supercritical CO₂ exposure," *Fuel*, vol. 184, pp. 289–303, 2016.
- [12] R. S. Middleton, J. W. Carey, R. P. Currier et al., "Shale gas and non-aqueous fracturing fluids: opportunities and challenges for supercritical CO₂," *Applied Energy*, vol. 147, pp. 500–509, 2015.
- [13] M. Godec, G. Koperina, R. Petrusak, and A. Oudinot, "Enhanced gas recovery and CO₂ storage in gas shales: a summary review of its status and potential," *Energy Procedia*, vol. 63, pp. 5849–5857, 2014.
- [14] Z. Zhai, X. Wang, X. Jin, L. Sun, J. Li, and D. Cao, "Adsorption and diffusion of shale gas reservoirs in modeled clay minerals at different geological depths," *Energy & Fuels*, vol. 28, no. 12, pp. 7467–7473, 2014.

- [15] T. F. T. Rexer, M. J. Benham, A. C. Aplin, and K. M. Thomas, "Methane adsorption on shale under simulated geological temperature and pressure conditions," *Energy & Fuels*, vol. 27, no. 6, pp. 3099–3109, 2013.
- [16] P. Charoensuppanimit, S. A. Mohammad, and K. A. M. Gasem, "Measurements and modeling of gas adsorption on shales," *Energy & Fuels*, vol. 30, no. 3, pp. 2309–2319, 2016.
- [17] B. M. Krooss, R. Littke, B. Müller, J. Frielingsdorf, K. Schwochau, and E. F. Idiz, "Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations," *Chemical Geology*, vol. 126, no. 3–4, pp. 291–318, 1995.
- [18] W. Kalkreuth, M. Holz, J. Levandowski et al., "The coalbed methane (CBM) potential and CO₂ storage capacity of the Santa Terezinha Coalfield, Paraná Basin, Brazil – 3D modelling, and coal and carbonaceous shale characteristics and related desorption and adsorption capacities in samples from exploration borehole CBM001-ST-RS," *Energy Exploration & Exploitation*, vol. 31, no. 4, pp. 485–527, 2013.
- [19] R. M. Bustin, A. M. M. Bustin, A. Cui, D. Ross, and V. M. Pathi, "Impact of shale properties on pore structure and storage characteristics," in *SPE Shale Gas Production Conference*, p. 28, Fort Worth, Texas, USA, 2008.
- [20] L. Huang, Z. Ning, Q. Wang et al., "Effect of organic type and moisture on CO₂/CH₄ competitive adsorption in kerogen with implications for CO₂ sequestration and enhanced CH₄ recovery," *Applied Energy*, vol. 210, pp. 28–43, 2018.
- [21] B. Yan, Y. Wang, and J. E. Killough, "Beyond dual-porosity modeling for the simulation of complex flow mechanisms in shale reservoirs," *Computational Geosciences*, vol. 20, no. 1, pp. 69–91, 2016.
- [22] D. J. K. Ross and R. M. Bustin, "The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs," *Marine and Petroleum Geology*, vol. 26, no. 6, pp. 916–927, 2009.
- [23] A. Hamza, I. A. Hussein, M. J. Al-Marri, M. Mahmoud, R. Shawabkeh, and S. Aparicio, "CO₂ enhanced gas recovery and sequestration in depleted gas reservoirs: a review," *Journal of Petroleum Science and Engineering*, vol. 196, p. 107685, 2021.
- [24] S. Rani, E. Padmanabhan, and B. K. Prusty, "Review of gas adsorption in shales for enhanced methane recovery and CO₂ storage," *Journal of Petroleum Science and Engineering*, vol. 175, pp. 634–643, 2019.
- [25] A. Tinni, C. H. Sondergeld, and C. S. Rai, "Hydrocarbon storage mechanism in shale reservoirs and impact on hydrocarbon production," in *Proceedings of the 5th Unconventional Resources Technology Conference*, pp. 3598–3605, Austin, Texas, 2017.
- [26] S. M. Kang, E. Fathi, R. J. Ambrose, I. Y. Akkutlu, and R. F. Sigal, "Carbon dioxide storage capacity of organic-rich shales," *SPE Journal*, vol. 16, no. 4, pp. 842–855, 2011.
- [27] S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, "On a theory of the van der Waals adsorption of gases," *Journal of the American Chemical Society*, vol. 62, no. 7, pp. 1723–1732, 1940.
- [28] J.-G. Choi, D. D. Do, and H. D. Do, "Surface diffusion of adsorbed molecules in porous media: monolayer, multilayer, and capillary condensation regimes," *Industrial & Engineering Chemistry Research*, vol. 40, no. 19, pp. 4005–4031, 2001.
- [29] P. Weniger, W. Kalkreuth, A. Busch, and B. M. Krooss, "High-pressure methane and carbon dioxide sorption on coal and shale samples from the Parana Basin, Brazil," *International Journal of Coal Geology*, vol. 84, no. 3–4, pp. 190–205, 2010.
- [30] X.-C. Lu, F.-C. Li, and A. T. Watson, "Adsorption studies of natural gas storage in Devonian shales," *SPE Formation Evaluation*, vol. 10, no. 2, pp. 109–113, 2013.
- [31] Y. Liu and J. Wilcox, "CO₂ adsorption on carbon models of organic constituents of gas shale and coal," *Environmental Science & Technology*, vol. 45, no. 2, pp. 809–814, 2011.
- [32] I. Klewiah, D. S. Berawala, H. C. Alexander Walker, P. Ø. Andersen, and P. H. Nadeau, "Review of experimental sorption studies of CO₂ and CH₄ in shales," *Journal of Natural Gas Science and Engineering*, vol. 73, p. 103045, 2020.
- [33] T. C. Ruppel, C. T. Grein, and D. Bienstock, "Adsorption of methane/ethane mixtures on dry coal at elevated pressure," *Fuel*, vol. 51, no. 4, pp. 297–303, 1972.
- [34] R. Humayun and D. L. Tomasko, "High-resolution adsorption isotherms of supercritical carbon dioxide on activated carbon," *AIChE Journal*, vol. 46, no. 10, pp. 2065–2075, 2000.
- [35] T. Zhang, G. S. Ellis, S. C. Ruppel, K. Milliken, and R. Yang, "Effect of organic-matter type and thermal maturity on methane adsorption in shale-gas systems," *Organic Geochemistry*, vol. 47, pp. 120–131, 2012.
- [36] D. J. K. Ross and R. M. Bustin, "Shale gas potential of the lower Jurassic Gordondale member, northeastern British Columbia, Canada," *Bulletin of Canadian Petroleum Geology*, vol. 55, no. 1, pp. 51–75, 2007.
- [37] D. J. K. Ross and R. M. Bustin, "Impact of mass balance calculations on adsorption capacities in microporous shale gas reservoirs," *Fuel*, vol. 86, no. 17–18, pp. 2696–2706, 2007.
- [38] D. J. K. Ross and R. M. Bustin, "Characterizing the shale gas resource potential of Devonian–Mississippian strata in the Western Canada sedimentary basin: application of an integrated formation evaluation," *AAPG Bulletin*, vol. 92, no. 1, pp. 87–125, 2008.
- [39] S. Wang, Z. Song, T. Cao, and X. Song, "The methane sorption capacity of Paleozoic shales from the Sichuan Basin, China," *Marine and Petroleum Geology*, vol. 44, pp. 112–119, 2013.
- [40] R. Heller and M. Zoback, "Adsorption of methane and carbon dioxide on gas shale and pure mineral samples," *Journal of Unconventional Oil and Gas Resources*, vol. 8, pp. 14–24, 2014.
- [41] L. Hong, J. Jain, V. Romanov et al., "An investigation of factors affecting the interaction of CO₂ and CH₄ on shale in Appalachian Basin," *Journal of Unconventional Oil and Gas Resources*, vol. 14, pp. 99–112, 2016.
- [42] O. P. Ortiz Cancino, D. Pino Pérez, M. Pozo, and D. Bessieres, "Adsorption of pure CO₂ and a CO₂/CH₄ mixture on a black shale sample: manometry and microcalorimetry measurements," *Journal of Petroleum Science and Engineering*, vol. 159, pp. 307–313, 2017.
- [43] S. Zhou, H. Xue, Y. Ning, W. Guo, and Q. Zhang, "Experimental study of supercritical methane adsorption in Longmaxi shale: insights into the density of adsorbed methane," *Fuel*, vol. 211, pp. 140–148, 2018.
- [44] B. C. Nuttal, C. Eble, R. M. Bustin, and J. A. Drahozal, "Analysis of Devonian black shales in Kentucky for potential carbon dioxide sequestration and enhanced natural gas

- production,” in *Greenhouse Gas Control Technologies*, pp. 2225–2228, Elsevier Science Ltd, Oxford, UK, 2005.
- [45] M. Gasparik, T. F. T. Rexer, A. C. Aplin et al., “First international inter-laboratory comparison of high-pressure CH₄, CO₂ and C₂H₆ sorption isotherms on carbonaceous shales,” *International Journal of Coal Geology*, vol. 132, pp. 131–146, 2014.
- [46] T. Cao, Z. Song, S. Wang, X. Cao, Y. Li, and J. Xia, “Characterizing the pore structure in the Silurian and Permian shales of the Sichuan Basin, China,” *Marine and Petroleum Geology*, vol. 61, pp. 140–150, 2015.
- [47] M. Vandenbroucke and C. Largeau, “Kerogen origin, evolution and structure,” *Organic Geochemistry*, vol. 38, no. 5, pp. 719–833, 2007.
- [48] J. C. Glorioso and A. J. Rattia, “Unconventional reservoirs: basic petrophysical concepts for shale gas,” in *SPE/EAGE European Unconventional Resources Conference and Exhibition*, p. 38, Vienna, Austria, 2012.
- [49] J. S. Seewald, “Organic–inorganic interactions in petroleum-producing sedimentary basins,” *Nature*, vol. 426, no. 6964, pp. 327–333, 2003.
- [50] G. R. L. Chalmers and R. M. Bustin, “Lower Cretaceous gas shales in northeastern British Columbia, part I: geological controls on methane sorption capacity,” *Bulletin of Canadian Petroleum Geology*, vol. 56, no. 1, pp. 1–21, 2008.
- [51] D. M. Jarvie, R. J. Hill, T. E. Ruble, and R. M. Pollastro, “Unconventional shale-gas systems: the Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment,” *AAPG Bulletin*, vol. 91, no. 4, pp. 475–499, 2007.
- [52] C. H. Sondergeld, K. E. Newsham, J. T. Comisky, M. C. Rice, and C. S. Rai, “Petrophysical considerations in evaluating and producing shale gas resources,” in *SPE Unconventional Gas Conference*, p. 34, Pittsburgh, PA, USA, 2010.
- [53] G. R. L. Chalmers and R. M. Bustin, “The organic matter distribution and methane capacity of the lower Cretaceous strata of Northeastern British Columbia, Canada,” *International Journal of Coal Geology*, vol. 70, no. 1–3, pp. 223–239, 2007.
- [54] R. M. Slatt and N. R. O'Brien, “Pore types in the Barnett and Woodford gas shales: contribution to understanding gas storage and migration pathways in fine-grained rocks,” *AAPG Bulletin*, vol. 95, no. 12, pp. 2017–2030, 2011.
- [55] J. L. Venaruzzo, C. Volzone, M. L. Rueda, and J. Ortega, “Modified bentonitic clay minerals as adsorbents of CO₂, CO₂ and SO₂ gases,” *Microporous and Mesoporous Materials*, vol. 56, no. 1, pp. 73–80, 2002.
- [56] K. L. Milliken, M. Rudnicki, D. N. Awwiller, and T. Zhang, “Organic matter-hosted pore system, Marcellus formation (Devonian), Pennsylvania,” *AAPG Bulletin*, vol. 97, no. 2, pp. 177–200, 2013.
- [57] M. Gasparik, A. Ghanizadeh, P. Bertier, Y. Gensterblum, S. Bouw, and B. M. Krooss, “High-pressure methane sorption isotherms of black shales from the Netherlands,” *Energy & Fuels*, vol. 26, no. 8, pp. 4995–5004, 2012.
- [58] L. Wang and Q. Yu, “The effect of moisture on the methane adsorption capacity of shales: a study case in the eastern Qaidam Basin in China,” *Journal of Hydrology*, vol. 542, pp. 487–505, 2016.
- [59] R. M. Bustin and C. R. Clarkson, “Geological controls on coalbed methane reservoir capacity and gas content,” *International Journal of Coal Geology*, vol. 38, no. 1–2, pp. 3–26, 1998.
- [60] Q. R. Passey, K. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, “From oil-prone source rock to gas-producing shale reservoir - geologic and petrophysical characterization of unconventional shale gas reservoirs,” in *International Oil and Gas Conference and Exhibition in China*, Society of Petroleum Engineers, Beijing, China, 2010.
- [61] T. F. Rexer, E. J. Mathia, A. C. Aplin, and K. M. Thomas, “High-pressure methane adsorption and characterization of pores in Posidonia shales and isolated kerogens,” *Energy & Fuels*, vol. 28, no. 5, pp. 2886–2901, 2014.
- [62] H. Xue, P. Jiang, R. Xu, B. Zhao, and Z. Shangwen, “Characterization of the reservoir in Lower Silurian and Lower Cambrian shale of south Sichuan Basin, China,” *Journal of Natural Gas Science and Engineering*, vol. 29, pp. 150–159, 2016.
- [63] H. Bi, Z. Jiang, J. Li et al., “The Ono–Kondo model and an experimental study on supercritical adsorption of shale gas: a case study on Longmaxi shale in southeastern Chongqing, China,” *Journal of Natural Gas Science and Engineering*, vol. 35, pp. 114–121, 2016.
- [64] Y. Wang, Y. Zhu, S. Liu, and R. Zhang, “Methane adsorption measurements and modeling for organic-rich marine shale samples,” *Fuel*, vol. 172, pp. 301–309, 2016.
- [65] A. Li, W. Ding, X. Zhou et al., “Investigation of the methane adsorption characteristics of marine shale: a case study of Lower Cambrian Qiongzhusi shale in eastern Yunnan Province, South China,” *Energy & Fuels*, vol. 31, no. 3, pp. 2625–2635, 2017.
- [66] A. Busch, S. Alles, Y. Gensterblum et al., “Carbon dioxide storage potential of shales,” *International Journal of Greenhouse Gas Control*, vol. 2, no. 3, pp. 297–308, 2008.
- [67] H. T. Schaefer, V.-A. Glezakou, A. T. Owen, S. Ramprasad, P. F. Martin, and B. P. McGrail, “Surface condensation of CO₂ onto kaolinite,” *Environmental Science & Technology Letters*, vol. 1, no. 2, pp. 142–145, 2013.
- [68] M. Gasparik, P. Bertier, Y. Gensterblum, A. Ghanizadeh, B. M. Krooss, and R. Littke, “Geological controls on the methane storage capacity in organic-rich shales,” *International Journal of Coal Geology*, vol. 123, pp. 34–51, 2014.
- [69] Y. Lu, X. Ao, J. Tang, Y. Jia, X. Zhang, and Y. Chen, “Swelling of shale in supercritical carbon dioxide,” *Journal of Natural Gas Science and Engineering*, vol. 30, pp. 268–275, 2016.
- [70] L. Huang, Z. Ning, Q. Wang et al., “Molecular simulation of adsorption behaviors of methane, carbon dioxide and their mixtures on kerogen: effect of kerogen maturity and moisture content,” *Fuel*, vol. 211, pp. 159–172, 2018.
- [71] I. Langmuir, “The adsorption of gases on plane surfaces of glass, mica and platinum,” *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.
- [72] S. Brunauer, P. H. Emmett, and E. Teller, “Adsorption of gases in multimolecular layers,” *Journal of the American Chemical Society*, vol. 60, no. 2, pp. 309–319, 1938.
- [73] R. O. Herzog, “Kapillarchemie, eine Darstellung der Chemie der Kolloide und verwandter Gebiete. Von Dr. Herbert Freundlich. Verlag der Akademischen Verlagsgesellschaft. Leipzig 1909. 591 Seiten. Preis 16,30 Mk., geb. 17,50 Mk.,” *Zeitschrift Für Elektrochemie Berichte Der Bunsengesellschaft Für Physikalische Chemie*, vol. 15, no. 23, pp. 948–948, 1909.
- [74] R. Sakurovs, S. Day, and S. Weir, “Relationships between the critical properties of gases and their high pressure sorption behavior on coals,” *Energy & Fuels*, vol. 24, no. 3, pp. 1781–1787, 2010.

- [75] R. Sakurovs, S. Day, and S. Weir, "Relationships between the sorption behaviour of methane, carbon dioxide, nitrogen and ethane on coals," *Fuel*, vol. 97, pp. 725–729, 2012.
- [76] H. Tian, T. Li, T. Zhang, and X. Xiao, "Characterization of methane adsorption on overmature Lower Silurian–Upper Ordovician shales in Sichuan Basin, southwest China: experimental results and geological implications," *International Journal of Coal Geology*, vol. 156, pp. 36–49, 2016.
- [77] X. Song, X. Lü, Y. Shen, S. Guo, and Y. Guan, "A modified supercritical Dubinin–Radushkevich model for the accurate estimation of high pressure methane adsorption on shales," *International Journal of Coal Geology*, vol. 193, pp. 1–15, 2018.
- [78] J. Hwang, L. Joss, and R. Pini, "Measuring and modelling supercritical adsorption of CO₂ and CH₄ on montmorillonite source clay," *Microporous and Mesoporous Materials*, vol. 273, pp. 107–121, 2019.
- [79] S. Zhou, H. Wang, H. Xue, W. Guo, and X. B. Li, "Supercritical methane adsorption on shale gas: mechanism and model," *Chinese Science Bulletin*, vol. 62, no. 35, pp. 4189–4200, 2017.
- [80] X. Luo, S. Wang, Z. Wang et al., "Adsorption of methane, carbon dioxide and their binary mixtures on Jurassic shale from the Qaidam Basin in China," *International Journal of Coal Geology*, vol. 150–151, pp. 210–223, 2015.
- [81] M. Godec, G. Koperina, R. Petrusak, and A. Oudinot, "Potential for enhanced gas recovery and CO₂ storage in the Marcellus Shale in the Eastern United States," *International Journal of Coal Geology*, vol. 118, pp. 95–104, 2013.
- [82] M. Pozo, D. Pino, and D. Bessieres, "Effect of thermal events on maturation and methane adsorption of Silurian black shales (Checa, Spain)," *Applied Clay Science*, vol. 136, pp. 208–218, 2017.
- [83] B. J. Sun, Y. L. Zhang, Q. J. Du, and Z. H. Shen, "Property evaluation of CO₂ adsorption and desorption on shale," *Journal of China University of Petroleum*, vol. 37, no. 5, pp. 95–99, 2013.
- [84] P. Chareonsuppanimit, S. A. Mohammad, R. L. Robinson, and K. A. M. Gasem, "High-pressure adsorption of gases on shales: measurements and modeling," *International Journal of Coal Geology*, vol. 95, pp. 34–46, 2012.
- [85] W. Guo, W. Xiong, S. Gao, Z. Hu, H. Liu, and R. Yu, "Impact of temperature on the isothermal adsorption/desorption of shale gas," *Petroleum Exploration and Development*, vol. 40, no. 4, pp. 514–519, 2013.
- [86] R. Zhang and S. Liu, "Experimental and theoretical characterization of methane and CO₂ sorption hysteresis in coals based on Langmuir desorption," *International Journal of Coal Geology*, vol. 171, pp. 49–60, 2017.
- [87] J. Chen, F. C. Wang, H. Liu, and H. A. Wu, "Molecular mechanism of adsorption/desorption hysteresis: dynamics of shale gas in nanopores," *Science China Physics, Mechanics & Astronomy*, vol. 60, no. 1, 2017.
- [88] D. Pino, F. Plantier, and D. Bessieres, "Experimental determination of the adsorption isotherms in gas mixtures under extended pressure and temperature range," *Journal of Thermal Analysis and Calorimetry*, vol. 117, no. 3, pp. 1469–1477, 2014.
- [89] Y. Ma, C. Yue, S. Li, X. Xu, and Y. Niu, "Study of CH₄ and CO₂ competitive adsorption on shale in Yibin, Sichuan Province of China," *Carbon Resources Conversion*, vol. 2, no. 1, pp. 35–42, 2019.
- [90] Z. Yang, Z. Dong, L. Wang et al., "Experimental study on selective adsorption/desorption of CO₂ and CH₄ behaviors on shale under a high-pressure condition," *Energy & Fuels*, vol. 32, no. 9, pp. 9255–9262, 2018.
- [91] R. Qi, Z. Ning, Q. Wang et al., "Sorption of methane, carbon dioxide, and their mixtures on shales from Sichuan Basin, China," *Energy & Fuels*, vol. 32, no. 3, pp. 2926–2940, 2018.
- [92] B. Liu, C. Qi, T. Mai et al., "Competitive adsorption and diffusion of CH₄/CO₂ binary mixture within shale organic nanochannels," *Journal of Natural Gas Science and Engineering*, vol. 53, pp. 329–336, 2018.
- [93] P. Huo, D. Zhang, Z. Yang, W. Li, J. Zhang, and S. Jia, "CO₂ geological sequestration: displacement behavior of shale gas methane by carbon dioxide injection," *International Journal of Greenhouse Gas Control*, vol. 66, pp. 48–59, 2017.
- [94] J. Liu, Y. Yao, D. Liu, and D. Elsworth, "Experimental evaluation of CO₂ enhanced recovery of adsorbed-gas from shale," *International Journal of Coal Geology*, vol. 179, pp. 211–218, 2017.
- [95] G. Zhao and C. Wang, "Influence of CO₂ on the adsorption of CH₄ on shale using low-field nuclear magnetic resonance technique," *Fuel*, vol. 238, pp. 51–58, 2019.
- [96] J.-J. Shieh and T. S. Chung, "Gas permeability, diffusivity, and solubility of poly(4-vinylpyridine) film," *Journal of Polymer Science Part B: Polymer Physics*, vol. 37, no. 20, pp. 2851–2861, 1999.
- [97] Y. Lan, Z. Yang, P. Wang, Y. Yan, L. Zhang, and J. Ran, "A review of microscopic seepage mechanism for shale gas extracted by supercritical CO₂ flooding," *Fuel*, vol. 238, pp. 412–424, 2019.
- [98] H. Sui and J. Yao, "Effect of surface chemistry for CH₄/CO₂ adsorption in kerogen: a molecular simulation study," *Journal of Natural Gas Science and Engineering*, vol. 31, pp. 738–746, 2016.
- [99] H. Sui and J. Yao, "Molecular simulation of CO₂/CH₄ competitive adsorption in kerogen," *Journal of China University of Petroleum*, vol. 40, no. 2, pp. 147–154, 2016.
- [100] H. Wang, G. Li, and Z. Shen, "A feasibility analysis on shale gas exploitation with supercritical carbon dioxide," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 34, no. 15, pp. 1426–1435, 2012.
- [101] J. Zhou, Q. Mao, and K. H. Luo, "Effects of moisture and salinity on methane adsorption in kerogen: a molecular simulation study," *Energy & Fuels*, vol. 33, no. 6, pp. 5368–5376, 2019.
- [102] J. Zhou, Z. Jin, and K. H. Luo, "Effects of moisture contents on shale gas recovery and CO₂ sequestration," *Langmuir*, vol. 35, no. 26, pp. 8716–8725, 2019.
- [103] J. Zhou, Z. Jin, and K. H. Luo, "The role of brine in gas adsorption and dissolution in kerogen nanopores for enhanced gas recovery and CO₂ sequestration," *Chemical Engineering Journal*, vol. 399, p. 125704, 2020.
- [104] G. N. Okolo, R. C. Everson, H. W. J. P. Neomagus, R. Sakurovs, M. Grigore, and J. R. Bunt, "The carbon dioxide, methane and nitrogen high-pressure sorption properties of South African bituminous coals," *International Journal of Coal Geology*, vol. 209, pp. 40–53, 2019.
- [105] A. Liquide, *Physical Properties of Gases*, Air Liquide Gas Encyclopedia, 2017.
- [106] D. E. Diller, "The Clausius-Mossotti functions (molar polarizabilities) of pure compressed gaseous and liquid methane,

- ethane, propane, butanes, and nitrogen,” *Cryogenics*, vol. 14, no. 4, pp. 215–216, 1974.
- [107] G. O. Wood, “Affinity coefficients of the Polanyi/Dubinin adsorption isotherm equations: a review with compilations and correlations,” *Carbon*, vol. 39, no. 3, pp. 343–356, 2001.
- [108] R. Z. Jiang, Y. Wa, and J.-f. Ji, “The new model for matrix and fracture permeability in shale reservoir,” *Natural Gas Geoscience*, vol. 25, no. 6, pp. 934–939, 2014.
- [109] S. Roy, R. Raju, H. F. Chuang, B. A. Cruden, and M. Meyyappan, “Modeling gas flow through microchannels and nanopores,” *Journal of Applied Physics*, vol. 93, no. 8, pp. 4870–4879, 2003.
- [110] D. Tzoulaki, L. Heinke, H. Lim et al., “Assessing surface permeabilities from transient guest profiles in nanoporous host materials,” *Angewandte Chemie International Edition*, vol. 48, no. 19, pp. 3525–3528, 2009.
- [111] A. S. Ziarani and R. Aguilera, “Knudsen’s permeability correction for tight porous media,” *Transport in Porous Media*, vol. 91, no. 1, pp. 239–260, 2012.
- [112] G. Karniadakis, A. Beşkök, and N. Aluru, *Microflows and Nanoflows : Fundamentals and Simulation*, Springer, New York, NY, USA, 2005.
- [113] R. K. Agarwal, K.-Y. Yun, and R. Balakrishnan, “Beyond Navier–Stokes: Burnett equations for flows in the continuum–transition regime,” *Physics of Fluids*, vol. 13, no. 10, pp. 3061–3085, 2001.
- [114] F. Javadpour, D. Fisher, and M. Unsworth, “Nanoscale gas flow in shale gas sediments,” *Journal of Canadian Petroleum Technology*, vol. 46, no. 10, 2013.
- [115] F. Javadpour, “Nanopores and apparent permeability of gas flow in mudrocks (shales and siltstone),” *Journal of Canadian Petroleum Technology*, vol. 48, no. 8, pp. 16–21, 2009.
- [116] C. M. Freeman, G. J. Moridis, and T. A. Blasingame, “A numerical study of microscale flow behavior in tight gas and shale gas reservoir systems,” *Transport in Porous Media*, vol. 90, no. 1, pp. 253–268, 2011.
- [117] F. P. Wang and R. M. Reed, “Pore networks and fluid flow in gas shales,” in *SPE Annual Technical Conference and Exhibition*, p. 8, New Orleans, LA, USA, 2009.
- [118] X. Li, J. Fan, H. Yu, Y. B. Zhu, and H. A. Wu, “Lattice Boltzmann method simulations about shale gas flow in contracting nano-channels,” *International Journal of Heat and Mass Transfer*, vol. 122, pp. 1210–1221, 2018.
- [119] H. Sun, J. Yao, D.-y. Fan, C.-c. Wang, and Z.-x. Sun, “Gas transport mode criteria in ultra-tight porous media,” *International Journal of Heat and Mass Transfer*, vol. 83, pp. 192–199, 2015.
- [120] W. Song, J. Yao, J. Ma, G. Couples, and Y. Li, “Assessing relative contributions of transport mechanisms and real gas properties to gas flow in nanoscale organic pores in shales by pore network modelling,” *International Journal of Heat and Mass Transfer*, vol. 113, pp. 524–537, 2017.
- [121] D. D. Mamora and J. G. Seo, “Enhanced gas recovery by carbon dioxide sequestration in depleted gas reservoirs,” in *SPE Annual Technical Conference*, pp. 1–9, San Antonio, Texas, USA, 2002, SPE-77347-MS.
- [122] S. Liu, Y. Zhang, W. Xing et al., “Laboratory experiment of CO₂–CH₄ displacement and dispersion in sandpicks in enhanced gas recovery,” *Journal of Natural Gas Science and Engineering*, vol. 26, pp. 1585–1594, 2015.
- [123] A. Honari, B. Bijeljic, M. L. Johns, and E. F. May, “Enhanced gas recovery with CO₂ sequestration: the effect of medium heterogeneity on the dispersion of supercritical CO₂–CH₄,” *International Journal of Greenhouse Gas Control*, vol. 39, pp. 39–50, 2015.
- [124] Y. Zhang, S. Liu, L. Wang et al., “In situ measurement of the dispersion coefficient of liquid/supercritical CO₂–CH₄ in a sandpack using CT,” *RSC Advances*, vol. 6, no. 48, pp. 42367–42376, 2016.
- [125] J.-Q. Shi, S. Mazumder, K.-H. Wolf, and S. Durucan, “Competitive methane desorption by supercritical CO₂ injection in coal,” *Transport in Porous Media*, vol. 75, no. 1, pp. 35–54, 2008.
- [126] F. Zhou, F. Hussain, and Y. Cinar, “Injecting pure N₂ and CO₂ to coal for enhanced coalbed methane: experimental observations and numerical simulation,” *International Journal of Coal Geology*, vol. 116–117, pp. 53–62, 2013.
- [127] L. Wang, Z. Wang, K. Li, and H. Chen, “Comparison of enhanced coalbed methane recovery by pure N₂ and CO₂ injection: experimental observations and numerical simulation,” *Journal of Natural Gas Science and Engineering*, vol. 23, pp. 363–372, 2015.
- [128] S. Mazumder, K. H. A. A. Wolf, P. van Hemert, and A. Busch, “Laboratory experiments on environmental friendly means to improve coalbed methane production by carbon dioxide/flue gas injection,” *Transport in Porous Media*, vol. 75, no. 1, pp. 63–92, 2008.
- [129] X.-D. Du, M. Gu, S. Duan, and X.-F. Xian, “Investigation of CO₂–CH₄ displacement and transport in shale for enhanced shale gas recovery and CO₂ sequestration,” *Journal of Energy Resources Technology*, vol. 139, no. 1, 2017.
- [130] X. Du, M. Gu, S. Duan, and X. Xian, “The influences of CO₂ injection pressure on CO₂ dispersion and the mechanism of CO₂–CH₄ displacement in shale,” *Journal of Energy Resources Technology*, vol. 140, no. 1, 2018.
- [131] X. Du, M. Gu, Z. Liu, Y. Zhao, F. Sun, and T. Wu, “Enhanced shale gas recovery by the injections of CO₂, N₂, and CO₂/N₂ mixture gases,” *Energy & Fuels*, vol. 33, no. 6, pp. 5091–5101, 2019.
- [132] J. Shi, L. Gong, S. Sun, Z. Huang, B. Ding, and J. Yao, “Competitive adsorption phenomenon in shale gas displacement processes,” *RSC Advances*, vol. 9, no. 44, pp. 25326–25335, 2019.