

## Review Article

# Study on Competitive Adsorption and Displacing Properties of CO<sub>2</sub> Enhanced Shale Gas Recovery: Advances and Challenges

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Received 9 October 2020; Revised 15 November 2020; Accepted 29 November 2020; Published 23 December 2020

Academic Editor: Guanglong Sheng

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CO<sub>2</sub> enhanced shale gas recovery (CO<sub>2</sub>-ESGR) draws worldwide attentions in recent years with having significant environmental benefit of CO<sub>2</sub> 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 CO<sub>2</sub>/CH<sub>4</sub>, and displacement of CO<sub>2</sub>-CH<sub>4</sub> in shale in the process of CO<sub>2</sub>-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 CO<sub>2</sub> and the interaction of CO<sub>2</sub> with shale matrix. Shale matrix shows a stronger affinity with CO<sub>2</sub>, and thus, adsorption capacity of CO<sub>2</sub> is larger than that of CH<sub>4</sub> even with the coexistence of CO<sub>2</sub>-CH<sub>4</sub> mixture. Displacement experiments of CO<sub>2</sub>-CH<sub>4</sub> in shale proved that shale gas recovery is enhanced by the competitive adsorption of CO<sub>2</sub> to CH<sub>4</sub>. Although the competitive adsorption mechanism is preliminary revealed, some challenges still exist. Competitive adsorption behavior is not fully understood in the coexistence of CO<sub>2</sub> and CH<sub>4</sub> components, and more experiment and model studies on adsorption of CO<sub>2</sub>-CH<sub>4</sub> mixtures need to be conducted under field conditions. Coupling of competitive adsorption with displacing flow is key factor for CO<sub>2</sub>-ESGR but not comprehensively studied. More displacement experiments of CO<sub>2</sub>-CH<sub>4</sub> in shale are required for revealing the mechanism of flow and transport of gas in CO<sub>2</sub>-ESGR.

## 1. Introduction

Due to increasing combustion of fossil fuels and the ensuing large-scale CO<sub>2</sub> emissions, the high level of CO<sub>2</sub> 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]. CO<sub>2</sub> capture, utilization, and storage (CCUS) technology is a promising and practical CO<sub>2</sub> mitigation technology by injecting the captured CO<sub>2</sub> 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, CO<sub>2</sub> fracturing has many advantages such as reducing fracturing pressure, reducing flow blockage, and avoiding reservoir damage and pollution [6, 12]. The conception of CO<sub>2</sub> enhanced shale gas recovery (CO<sub>2</sub>-ESGR) technology comes out by combining CO<sub>2</sub> fracturing and CO<sub>2</sub> injection for shale gas exploitation. CO<sub>2</sub> replaces the adsorbed CH<sub>4</sub> in shale matrix (kerogen or clay) through competitive adsorption and displaces the free CH<sub>4</sub> in the fractured pores during the process of CO<sub>2</sub>-ESGR, thereby increasing the recovery of shale gas. Notably, CO<sub>2</sub>-ESGR is one of the promising CCUS technologies to store CO<sub>2</sub> into the shale formation for greenhouse gas emission reduction [13]. Thus, CO<sub>2</sub>-ESGR has great application potential for both the economic benefit of efficient exploitation of shale gas reservoirs and the simultaneous environmental benefit of CO<sub>2</sub> mitigation.

CO<sub>2</sub>-ESGR contains several processes, such as shale fracturing, CO<sub>2</sub> displacement of the free CH<sub>4</sub> in pore and fractures, CH<sub>4</sub> desorption and CO<sub>2</sub> competitive adsorption, and CO<sub>2</sub> geological storage. The schematic diagram of CO<sub>2</sub>-ESGR is shown in Figure 1. Therefore, in order to achieve effective development of CO<sub>2</sub>-ESGR technology, some relevant key scientific problems must be solved, including mechanism of CH<sub>4</sub> adsorption/desorption, CO<sub>2</sub>/CH<sub>4</sub> competitive adsorption mechanism in shale matrix, and CO<sub>2</sub> displacement CH<sub>4</sub> flow and mass transfer mechanism. The adsorption/desorption characteristic of single-component gas (CH<sub>4</sub> or CO<sub>2</sub>) in shale has also been fundamentally studied [14–16]. Among these key scientific problems, mechanism of CO<sub>2</sub>/CH<sub>4</sub> competitive adsorption in shale matrix and flow and mass transfer in the displacement of CO<sub>2</sub>-CH<sub>4</sub> 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 CO<sub>2</sub> replacing and displacing shale gas in CO<sub>2</sub>-ESGR, link the study on adsorption/desorption of CO<sub>2</sub>/CH<sub>4</sub> in shale and flow characteristics of CO<sub>2</sub> displacing CH<sub>4</sub>. The advances on competitive adsorption of CO<sub>2</sub>/CH<sub>4</sub> during CO<sub>2</sub> displacing CH<sub>4</sub> in shale related to CO<sub>2</sub>-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 CH<sub>4</sub> (>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 CH<sub>4</sub> 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

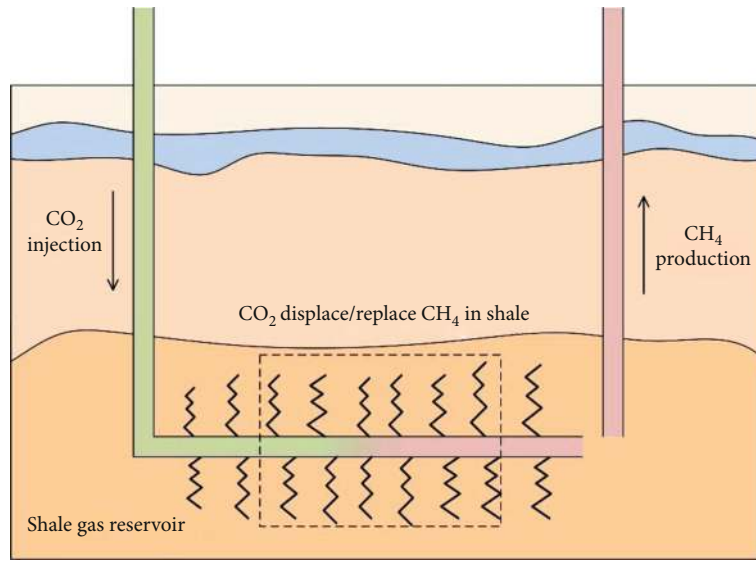
of gas storage. Thus, adsorption/desorption characteristics of CH<sub>4</sub> in shale play a key role in the determination of economic feasibility and exploration mode of shale gas reservoirs. The knowledge of gas storage and transport mechanisms related to adsorption is required for resource quantification 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.

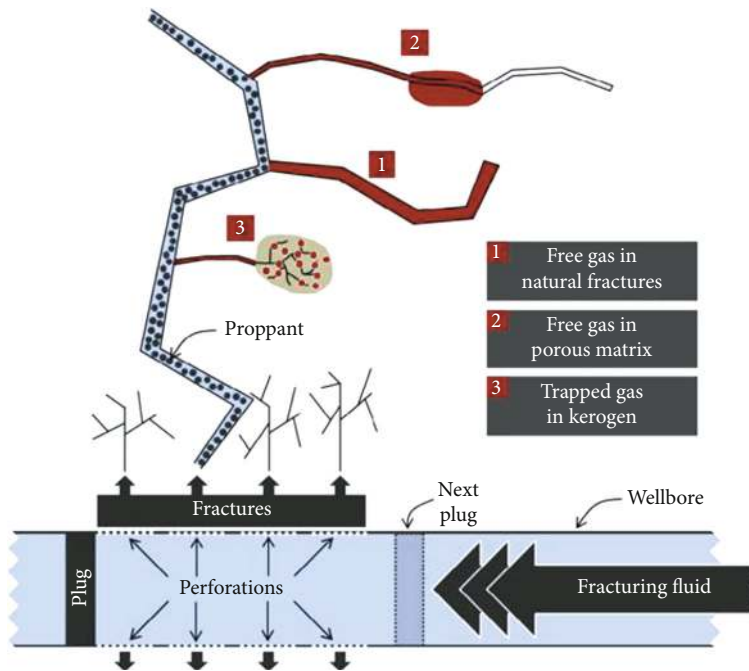
The gas adsorption characteristics in shale are usually evaluated by the measurement of adsorption isotherms in laboratory, which involves measuring the uptake or release of either gas species on a shale sample at certain temperature and pressure conditions [29–32]. Adsorption isotherm curves are commonly 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CO<sub>2</sub> enhanced shale gas recovery; (b) schematic diagram of CO<sub>2</sub> displacing/replacing CH<sub>4</sub> in shale during CO<sub>2</sub> fracturing for enhanced shale gas recovery [12].

CH<sub>4</sub> in shale is proportional to the organic matter content, and the larger TOC can improve the adsorption capacity of CH<sub>4</sub>. 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 CH<sub>4</sub> 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.

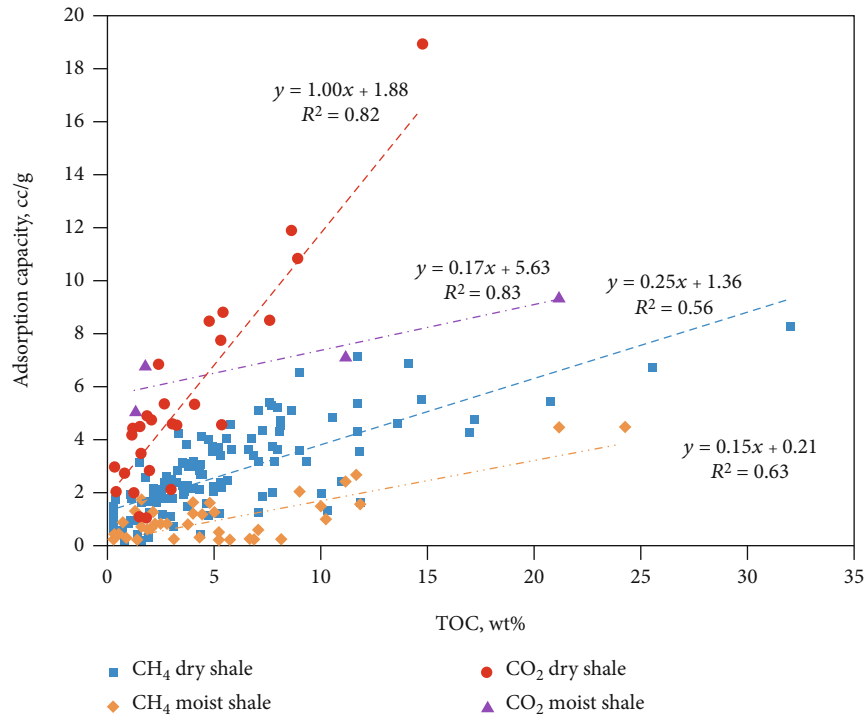


FIGURE 2: Correlation between TOC and CH<sub>4</sub> and CO<sub>2</sub> sorption capacity in dry and moisture shales [32]. Experimental data points are selected from literature [22, 29, 35–45].

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<sub>4</sub> 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<sub>4</sub> 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<sub>2</sub> adsorption [29]. Nevertheless, more researchers have proven that the mineral components have appreciable sorption capacity for both CH<sub>4</sub> and CO<sub>2</sub> [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<sub>4</sub> 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<sub>4</sub> 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 $\text{CO}_2$ and $\text{CH}_4$ in Shale.

Due to the physical properties difference,  $\text{CO}_2$  and  $\text{CH}_4$  have significantly different adsorption behavior in shale. The typical adsorption isotherms for  $\text{CH}_4$  and  $\text{CO}_2$  have been studied by Weniger et al. [29], shown in Figure 3. Under different TOC condition, the excess adsorption of  $\text{CH}_4$  in shale consistently increases with pressure and gradually reach a constant value at high pressures [32, 63–65]. The adsorption of  $\text{CO}_2$  is closely related to the phase state: in gas state, the excess adsorption of  $\text{CO}_2$  increases with pressure by having a larger increasing rate than  $\text{CH}_4$  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  $\text{CO}_2$  and  $\text{CH}_4$  has also been clearly reported in other experiments [45, 66–70].

Compared to  $\text{CH}_4$  adsorption in shale, some influencing factors have different performance for  $\text{CO}_2$  adsorption in shale, which will be described as follows. Similar with  $\text{CH}_4$ ,  $\text{CO}_2$  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  $\text{CO}_2$  is much larger than that of  $\text{CH}_4$  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  $\text{CH}_4$  in the moist shale is lower than that in dry one;  $\text{CO}_2$  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  $\text{CO}_2$  and  $\text{CH}_4$  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  $\text{CO}_2$  and  $\text{CH}_4$ , 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  $\text{CH}_4$  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  $\text{CO}_2$  and -82.6°C and 4.6 MPa for  $\text{CH}_4$  [74, 75], and thereby,  $\text{CH}_4$  and  $\text{CO}_2$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  with different pore diameters, Zhou et al. [79] proved that the adsorption form of  $\text{CH}_4$  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 $\text{CH}_4$ and $\text{CO}_2$

The conception of  $\text{CO}_2$ -ESGR for shale gas exploitation has a unique promising potential through  $\text{CO}_2$  competitive adsorption to release the adsorbed  $\text{CH}_4$  from shale matrix into the fractures and cracks for production and thus to increase shale gas recovery [32]. Thus, the competitive adsorption of  $\text{CO}_2$  to  $\text{CH}_4$  in shale plays the key role on  $\text{CO}_2$ -ESGR. When  $\text{CO}_2$  injected into shale reservoir,  $\text{CO}_2$  will compete the adsorption sites on the inner surface of shale matrix with  $\text{CH}_4$ . Then, the desorption of  $\text{CH}_4$  and adsorption of  $\text{CO}_2$  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  $\text{CO}_2/\text{CH}_4$  Competitive Adsorption.** The competitive adsorption characteristics of

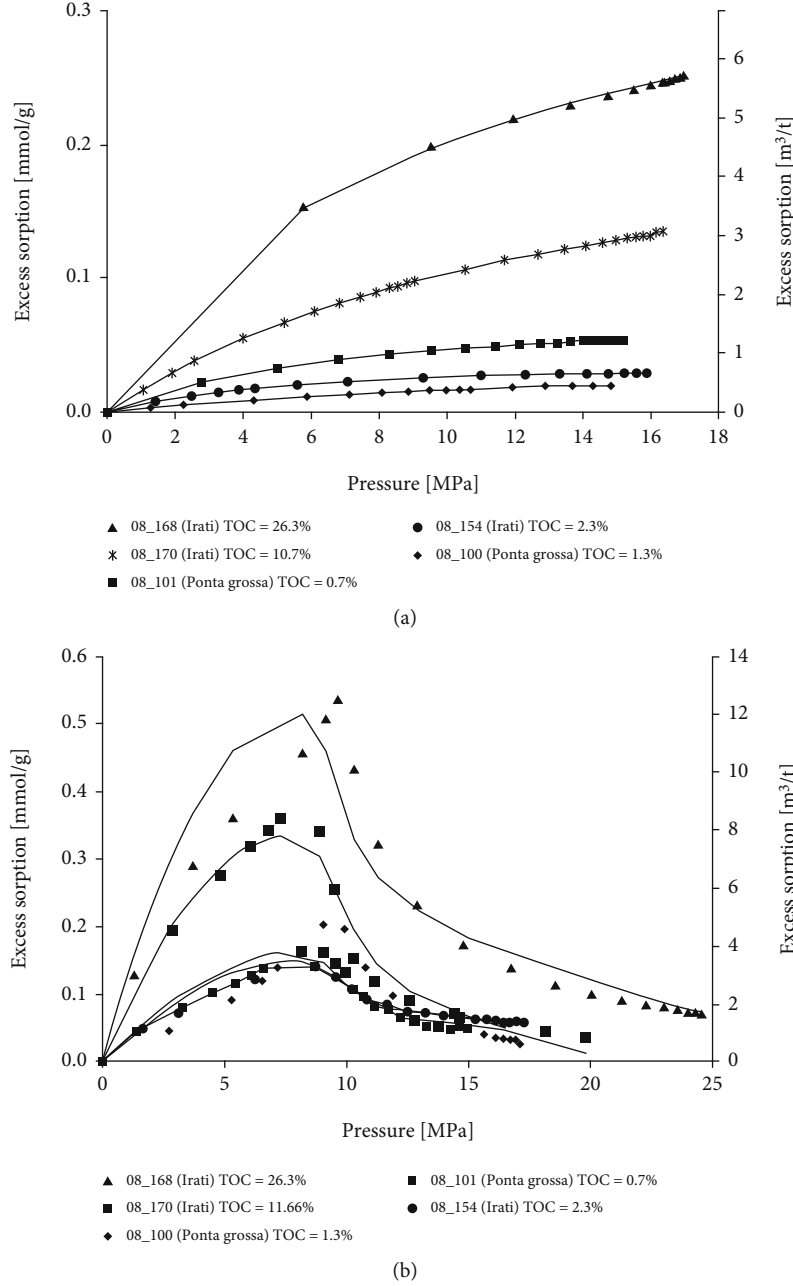


FIGURE 3: Adsorption isotherm (excess sorption vs. pressure) for (a)  $\text{CH}_4$  and (b)  $\text{CO}_2$  on crushed dry shale samples of the Parana Basin in Brazil at a temperature of  $45^\circ\text{C}$  [29].

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.

$\text{CO}_2$  to  $\text{CH}_4$  were initially investigated by comparative analysis of the adsorption behavior between single-component gas of  $\text{CO}_2$  and  $\text{CH}_4$ . Nuttall et al. [44] first observed that the adsorption capacity of pure  $\text{CO}_2$  is approximately 5 times greater than that of  $\text{CH}_4$  in Devonian black shales at the same conditions. The adsorption capacity of pure  $\text{CO}_2$  was also reported consistently higher than that of  $\text{CH}_4$  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  $\text{CO}_2$  and  $\text{CH}_4$ , reported the  $\text{CO}_2/\text{CH}_4$  adsorption ratio in the range of 1.3–10 for dry shale, and revealed moisture weakening the  $\text{CO}_2/\text{CH}_4$  adsorption ratio. Similar to  $\text{CH}_4$ , the

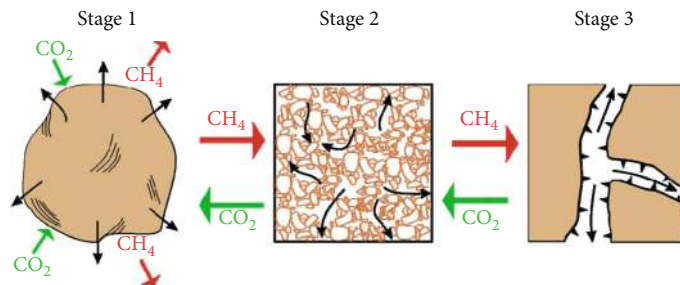


FIGURE 4: Schematic diagram of the competitive adsorption and transport of CO<sub>2</sub> and CH<sub>4</sub> in shales [13].

increase in pressure and organic carbon content contributes to adsorption capacity of CO<sub>2</sub> in shale, while the temperature is the opposite. Compared to CH<sub>4</sub>, the desorption process of CO<sub>2</sub> has an obvious hysteresis effect, which is conducive to long-term CO<sub>2</sub> storage [83, 85]. The moisture, matrix expansion, and pore throat size may affect the hysteresis of CO<sub>2</sub> desorption behavior, but the mechanism of CO<sub>2</sub> desorption hysteresis has not been thoroughly revealed [86, 87].

The adsorption experiments of CO<sub>2</sub>-CH<sub>4</sub> mixture system [42, 88–92] show that the greater adsorption affinity exists for CO<sub>2</sub> in shales than CH<sub>4</sub> even though sometimes CH<sub>4</sub> is preferentially adsorbed in the adsorption experiment of CO<sub>2</sub>-CH<sub>4</sub> mixture. It is revealed that CO<sub>2</sub> has a higher adsorption capacity in the coexistence of CO<sub>2</sub> and CH<sub>4</sub>, proving that competitive adsorption is beneficial to the implementation of CO<sub>2</sub>-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<sub>2</sub>/CH<sub>4</sub> in the mixture system may be smaller than that under condition of single-component adsorption. Thus, more experiments of CO<sub>2</sub>-CH<sub>4</sub> 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<sub>2</sub>-CH<sub>4</sub> mixture system, several researchers carried out dynamic competitive adsorption experiment on CO<sub>2</sub>-CH<sub>4</sub> exchange characteristics [93–95]. The competitive adsorption ratio and enhanced recovery of shale gas by injection of CO<sub>2</sub> were also proved by these dynamic experiments.

**3.2. Mechanism of CO<sub>2</sub>/CH<sub>4</sub> Competitive Adsorption.** As for the mechanism of competitive adsorption between CO<sub>2</sub> and CH<sub>4</sub> in shale, the competition for adsorption sites plays a key role on CO<sub>2</sub> replacing CH<sub>4</sub>. 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<sub>2</sub> and CH<sub>4</sub> [32]. The molecular characteristic difference between CO<sub>2</sub> and CH<sub>4</sub> is crucial: CH<sub>4</sub> molecule is tetrahedral geometry with a relative larger kinetic diameter of 3.80 Å, and CO<sub>2</sub> molecule is linear molecular with a smaller kinetic diameter of 3.30 Å [26, 74, 75, 96], shown in Table 2. Due to the smaller molecular size, CO<sub>2</sub> can easily access into

micro/nano-scale pores with smaller diameter which may be difficult for CH<sub>4</sub>, and thus, CO<sub>2</sub> is favourable to contact larger surface and adsorption sites in shale matrix [32, 97]. Moreover, CO<sub>2</sub> can interact more strongly with functional groups in kerogen because of higher quadrupole moment, and thus, CO<sub>2</sub> is more prone to physical adsorption caused by van der Waals force than CH<sub>4</sub> [26, 98, 99]. Zhao and Wang [95] revealed that the surface of shale organic matter has a stronger affinity for CO<sub>2</sub> than CH<sub>4</sub>, and then, CO<sub>2</sub> competes for adsorption sites to replace the adsorbed CH<sub>4</sub> on the surface of the matrix. The higher critical temperature of CO<sub>2</sub> also favour the competitive adsorption to replace CH<sub>4</sub> [97]. As an endothermic reaction, desorption process of CH<sub>4</sub> needs a relative lower of the adsorption heat than that of CO<sub>2</sub>, and thus, desorption of CH<sub>4</sub> from shale can be more easily realized in the coexisting CO<sub>2</sub> adsorption process. The unique supercritical properties of CO<sub>2</sub>, 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<sub>4</sub> [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<sub>2</sub>/CH<sub>4</sub> competitive adsorption. Huang et al. [20, 70] studied the competitive adsorption behavior of CO<sub>2</sub>/CH<sub>4</sub> in dry and moist realistic kerogen models of different organic types. The simulation results showed that the CO<sub>2</sub>/CH<sub>4</sub> adsorption selectivity increases with increasing CO<sub>2</sub> concentration at low pressure for kerogen models of higher maturity but decreases with CO<sub>2</sub> mole fraction for lower mature kerogen models. Specifically, CO<sub>2</sub>/CH<sub>4</sub> adsorption selectivity increases with the enterable pore volume fraction in the immature organic type. The CO<sub>2</sub>/CH<sub>4</sub> adsorption selectivity decreases first and then increases with the moisture content while the adsorption of CO<sub>2</sub> is more sensitive with moisture than that of CH<sub>4</sub>. However, moisture can potentially boost the displacement of CH<sub>4</sub> by CO<sub>2</sub> at certain conditions. Zhou et al. [101–103] also conducted a series of molecular simulations on CO<sub>2</sub> and CH<sub>4</sub> 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<sub>2</sub> injection in kerogen slit pores and analyzed the effect of moisture. CH<sub>4</sub>

TABLE 2: Physical properties and molecular parameters of CO<sub>2</sub> and CH<sub>4</sub> [104].

Property	CO <sub>2</sub>	CH <sub>4</sub>	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, $\rho_c$ (kg/m <sup>3</sup> )	467.6	162.7	[105]
Adsorbed phase density, $\rho_a$ (kg/m <sup>3</sup> )	1028	372	[74, 75]
Molar polarizability, $\alpha M$ (cm <sup>3</sup> /mol)	7.34	6.54	[106, 107]
Kinetic diameter, $\sigma_k$ (Å°)	3.30	3.80	[74, 75, 96]
Collision diameter, $\sigma_{col}$ (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 CO<sub>2</sub>-CH<sub>4</sub> mixture decreases with increasing moisture due to the accumulated H<sub>2</sub>O clusters impeding the pore filling of CH<sub>4</sub> in the kerogen slit pores. Compared to pressure drawdown, CO<sub>2</sub> injection can release CH<sub>4</sub> molecules in the adsorption layer; the CH<sub>4</sub> recovery ratio of CO<sub>2</sub> injection increases with the increasing moisture. Zhou et al. [103] found that the total uptake of CH<sub>4</sub> and CO<sub>2</sub>, including adsorption in kerogen surfaces and dissolution at kerogen/water interface and in water/brine, decreases linearly with increasing salinity. Salinity effects on CO<sub>2</sub> uptake are proved as complicated. The CO<sub>2</sub> adsorption decreases due to the pore volume in kerogen surfaces occupied by brine, but the remarkable enhancement in CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>/CH<sub>4</sub> is not very clear, especially under the condition of mixture. More related experiments and models study should be conducted.

## 4. Displacement of CH<sub>4</sub> by CO<sub>2</sub> in Shale

**4.1. Flow Mechanism in Shale.** CH<sub>4</sub>/CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 CH<sub>4</sub> 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 CO<sub>2</sub>-CH<sub>4</sub>.** As for the process of CO<sub>2</sub> displacing CH<sub>4</sub> in shale, the gas flow and mass



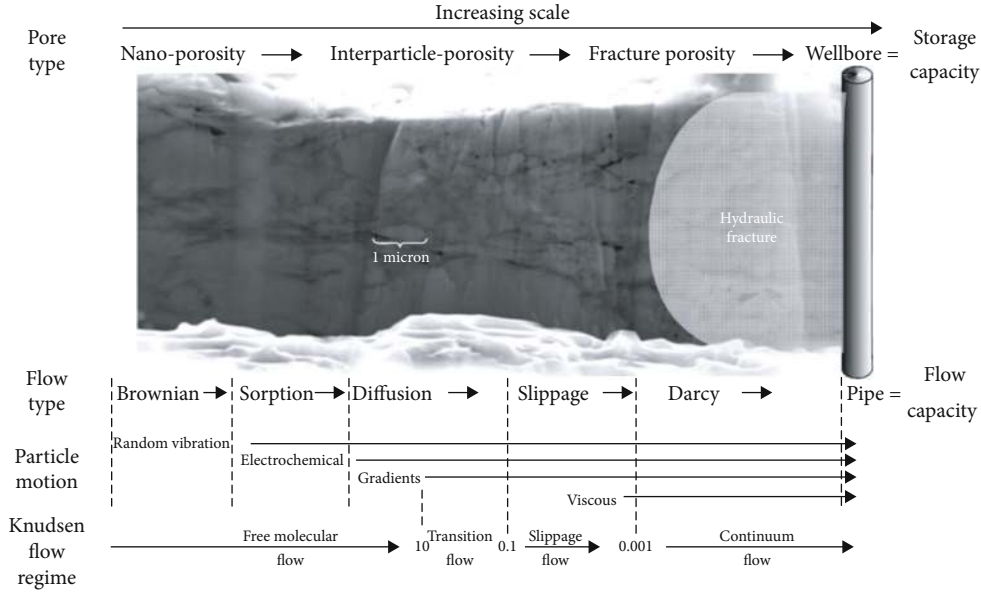


FIGURE 5: Multiscale migration mechanism of gas in shale [52].

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

Flow regime	$K_n$ range <sup>a,b</sup>	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 <sup>c</sup>	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 <sup>d</sup> , alternative methods are DSMC and lattice Boltzmann <sup>c</sup>	Usually occurs in shale formations where the pore throat radius is very small.

<sup>a</sup>This Knudsen number classification is taken from Karniadakis et al. [112]. <sup>b</sup>Some reference suggests ( $K_n < 0.001$ ) as a cut off for continuum flow [109]. <sup>c</sup>For more details, see Agarwal et al. [113]. <sup>d</sup>Knudsen's diffusion can coexist with bulk and surface diffusion.

transfer are more complicated than single-component gas flow. Different from  $\text{CH}_4$  flow in shale, the competitive adsorption of  $\text{CO}_2/\text{CH}_4$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CH}_4$  was enhanced by  $\text{CO}_2$  due to competitive adsorption effect with comparing  $\text{N}_2$  displacement experiments [126,

127]. It is also verified in the displacement experiments that the moisture can prevent the  $\text{CO}_2$  binding to adsorption sites and then affecting the displacement efficiency [128].

There are relatively few studies on the displacement study of  $\text{CO}_2$ - $\text{CH}_4$  and the dynamic competitive adsorption in shale related to  $\text{CO}_2$ -ESGR. Du et al. [129–131] conducted a series of  $\text{CO}_2$ - $\text{CH}_4$  displacement experiments in the crushed shale pack for the displacement properties and dispersion characteristics. Du et al. [129] first analyzed the  $\text{CH}_4$  recovery efficiency and  $\text{CO}_2$  storage efficiency in displacement experiments. The experimental results showed that  $\text{CO}_2$  has a larger dynamic adsorption rate and adsorption capacity, which ensures the feasibility of  $\text{CO}_2$ -ESGR. It is also found that the competitive adsorption between  $\text{CO}_2$  and  $\text{CH}_4$  will cause fluctuations in pore pressure, which in turn will enhance dispersion and produce a wider range of  $\text{CO}_2$ - $\text{CH}_4$  mixed phase regions. Du et al. [130] further explored the influence of  $\text{CO}_2$  injection pressure on the dispersion characteristics in  $\text{CO}_2$ - $\text{CH}_4$  displacement experiment. Based on the convective dispersion theory, it is found that  $\text{CO}_2$  diffusion is dominant under the condition of lower  $\text{CO}_2$  injection pressure, and the mass transfer coefficient and the miscible area increase with the increasing injection pressure, while the competitive adsorption between  $\text{CO}_2$  and  $\text{CH}_4$  is becoming obvious. The comparison of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2/\text{N}_2$  mixtures was also conducted; a higher  $\text{CH}_4$  recovery existed in  $\text{CO}_2$  displacement than that in  $\text{N}_2$  displacement [131]. The displacement efficient of  $\text{CH}_4$  by  $\text{CO}_2$  was also compared with  $\text{N}_2$  in simulation, and it is verified that competitive adsorption leads to a larger recovery for  $\text{CO}_2$  displacing shale gas [132].

## 5. Challenges and Opportunities

The adsorption/desorption of shale gas, competitive adsorption of  $\text{CO}_2$  to  $\text{CH}_4$ , 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  $\text{CO}_2$ -ESGR.

A lot of experimental and modelling studies on adsorption/desorption have been conducted in crushed shale samples, especially for  $\text{CH}_4$ , and the adsorption mechanism of  $\text{CH}_4$  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  $\text{CH}_4$ ,  $\text{CO}_2$  has different physical properties and different adsorption behaviors, especially in the supercritical. The adsorption mechanism of  $\text{CO}_2$  is not fully revealed, especially under supercritical state, and thus, more experiments and models research on  $\text{CO}_2$  adsorption/desorption are urgently needed.

The competitive adsorption of  $\text{CO}_2$  to  $\text{CH}_4$  is basically proved by a lot of comparative adsorption experiments of pure gas composition and some adsorption studies of  $\text{CO}_2$ -

$\text{CH}_4$  mixtures in shale. However, the competitive adsorption has different behavior in the adsorption experiments of single-component gas and  $\text{CO}_2$ - $\text{CH}_4$  mixture system. To quantitatively evaluate the competitive adsorption, adsorption ratio of  $\text{CO}_2/\text{CH}_4$  also shows different for the experiment of single-component gas and mixtures. The  $\text{CO}_2$ - $\text{CH}_4$  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  $\text{CO}_2$ - $\text{CH}_4$ . Considering the different properties between  $\text{CO}_2$  and  $\text{CH}_4$ , the competitive adsorption mechanism is qualitatively analyzed. However, how to accurately predict the adsorption  $\text{CO}_2$  or  $\text{CH}_4$  component in  $\text{CO}_2$ - $\text{CH}_4$  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  $\text{CO}_2$  to  $\text{CH}_4$  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  $\text{CO}_2$ -ESGR, the injection of  $\text{CO}_2$  makes the flow and gas transport more complicated. The mechanism of competitive adsorption of  $\text{CO}_2$  to  $\text{CH}_4$  coupled with flow and  $\text{CO}_2$ - $\text{CH}_4$  dispersion is not fully ascertained.  $\text{CO}_2$ - $\text{CH}_4$  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  $\text{CO}_2$ - $\text{CH}_4$  for  $\text{CO}_2$ -ESGR.

## 6. Conclusions

Due to both the environmental effect of  $\text{CO}_2$  geological storage and economic effect of shale gas exploitation,  $\text{CO}_2$  enhanced shale gas recovery ( $\text{CO}_2$ -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  $\text{CO}_2$ - $\text{CH}_4$  in shale related to  $\text{CO}_2$ -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.  $\text{CO}_2$  enhanced shale gas recovery has great potential to exploit shale gas reservoirs with permanently storing  $\text{CO}_2$  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 CO<sub>2</sub> in shale is much larger than that of CH<sub>4</sub> even with the coexistence of CO<sub>2</sub>-CH<sub>4</sub> mixture. Due to the unique properties of CO<sub>2</sub>, shale matrix shows a stronger affinity with CO<sub>2</sub>, and CO<sub>2</sub> can be more easily adsorbed on the inner surface of shale matrix than CH<sub>4</sub>
- (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 CO<sub>2</sub>-CH<sub>4</sub> is very complicated with mass transfer between two gases. Dynamic studies on displacement of CO<sub>2</sub>-CH<sub>4</sub> in shale prove that CH<sub>4</sub> 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 CH<sub>4</sub> and CO<sub>2</sub> 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 CO<sub>2</sub>-CH<sub>4</sub> adsorption experiments under field conditions, especially dynamic experiments, should be conducted to determine the CO<sub>2</sub>/CH<sub>4</sub> adsorption ratio. Corresponding, establishment of quantification model on competitive adsorption of CO<sub>2</sub> to CH<sub>4</sub> in shale should draw attentions in the future work
- (ix) Dynamic competitive adsorption coupling with flow in the displacement of CO<sub>2</sub>-CH<sub>4</sub> plays the key role on CO<sub>2</sub>-ESGR but is not fully understood. The future work should look into the coupling of various flow regime, competitive adsorption of CO<sub>2</sub>-CH<sub>4</sub>, convection dispersion, etc

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

This paper has been financially supported by the National Natural Science Foundation of China (51906256 and U1762216), the Fundamental Research Funds for the Central Universities (18CX02029A), and the Program for Chang-

jiang Scholars and Innovative Research Team in University of Ministry of China (IRT\_14R58), which are gratefully acknowledged.

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