

Adsorption of CO₂/CH₄ in shale organic nanoparticles: A molecular simulation study

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Keywords: Shale gas; Carbon dioxide; Adsorption; Molecular simulation

Abstract. Shale gas is a kind of unconventional gas, but it is difficult to exploit because of the low permeability and porosity of shale. In recent years, with the larger emission of CO₂, how to use CO₂ to enhance shale gas recovery (CO₂-ESGR) and sequester CO₂ effectively is a topic of common concern. Besides the experiment and theory, molecular simulation is another research method which can describe the competitive adsorption law of CH₄ and CO₂ in a more profound and microscopic way. In the current work, molecular simulations have been carried out using a grand canonical Monte Carlo method and molecular dynamics method to study the competitive adsorption of CH₄ and CO₂ in the carbon-based slit pores of a given width. The burial depth, composition and other factors were studied, and the density distribution of CH₄ and CO₂ in the pore and the adsorption selectivity of CO₂ over CH₄ are also analyzed. The results indicated that adsorption amount of CO₂ is almost constant, while CH₄ sorption is increasing with the increase of buried depth. Furthermore, under the same temperature and pressure, CO₂ has a higher adsorption capacity and isosteric heat. In the case of ratio of CH₄:CO₂=1:1, there is a large proportion of CO₂ in the pore wall. The CO₂ of adsorbate state is parallel to the pore surface. The higher CO₂ ratio, the larger selectivity of graphene for CO₂ relative to CH₄, which reflected the larger CO₂ adsorption capacity.

Introduction

The shale gas reservoir has smaller pore diameter and larger specific surface area. The adsorbed gas in the reservoir has a large proportion, it can account for 20%~80% of the total gas quantity [1]. Shale is comprised of various inorganic and organic materials. Numerous works found that total organic carbon (TOC) content is proportional to the CH₄ sorption [2-4]. It is believed that organic matter contains a lot of nano-pore (Fig. 1) and have strong affinity with CH₄. Since the difficulty of shale gas reservoir development, horizontal drilling and multi-stage hydraulic fracturing technologies are often used in the exploitation of shale gas. In a typical shale gas production process, it is considered that first

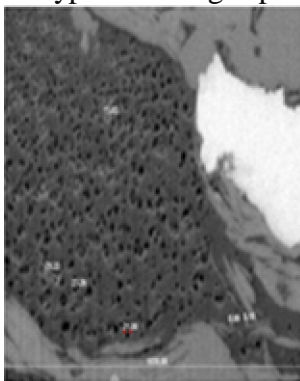


Fig.1 The nanopore structure of the shale matrix [5]

rapid production period of a typical length scale of under two years is corresponding to the free gas in fractures and large pores permeated out. However, the later production process is corresponding to the adsorbed gas because of the slow desorption at the small pore surfaces. Therefore, understanding the competitive adsorption of CH₄ and CO₂ in shale organic matter nanoparticles provides insight in

enhancing shale CH₄ recovery and mitigating global CO₂ emissions. Although CO₂ to enhance shale gas recovery technique has not been commercialized yet, attempts have been made to investigate the feasibility of the technique in shales.

Pierre Billemon et al. studied the sorption and isosteric heat of CH₄ and CO₂ in the graphene model, and analyzed the influence of water on gas adsorption[6]. Jin et al. studied the CH₄ and CO₂ density distribution in the montmorillonite pore and influence of pressure is discussed[7]. Sui and Yao investigated the adsorption of CH₄ and CO₂ in the organic kerogen, they found that Langmuir law suit to describe the adsorption of CH₄ and CO₂ in the pores of organic matter[8]. Wang et al. researched the CO₂ and CH₄ competitive adsorption in organic matter pores under certain geological conditions. Geothermal gradient and the pressure coefficient are taken into consideration. The results show that the pressure coefficient has a stronger effect on CH₄ adsorption, selectivity of CO₂ in organic matter model decrease with the increase of temperature and pressure[9]. In study by Jin and Firoozabadi, it is shown that effect of pressure on the sorption of n-butane/CH₄ and n-butane/CO₂ in the graphene slit pores[10]. Among the works mentioned above, many remarkable conclusions are drawn, but the sorption and configurations of CO₂/CH₄ in the pores for different ratios still need further discussion. This work investigates the relationship between buried depth, gas composition and CH₄/CO₂ sorption, the molecular configurations and adsorption selectivity of CO₂ over CH₄ in order to predict the feasibility for applying use CO₂ to enhance shale gas recovery and sequester CO₂ in depleted shale reservoirs.

Model and simulation methods

Three-layered graphene model is constructed (Fig. 2). The distance between each layer of graphene is 0.335 nm. The length in *x* and *y* direction is *L_x*=4.92 nm and *L_y*=4.26 nm respectively. Different values in the *z* direction simulate different pore sizes. The effective aperture is the distance of the inner molecule minus the diameter of the carbon atom. In this work, *z* of the graphene slit pore is set to 3 nm.



Fig. 2 Model of graphene slit pore

Using the Monte Carlo method (GCMC) to calculate the gas sorption. The force field selects COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies), which van der Waals potential force is calculated by LJ9-6 function (Eq. 1), where r_{ij}^0 is the distance at which the potential reaches its minimum, ϵ_{ij} is the depth of potential well, r_{ij} is the distance between the particles for like atoms pairs. For different atoms, the van der Waals parameters are calculated by Eq. (2) and Eq. (3). The sampling method is Metropolis. Electrostatic potential energy and van der

$$E_{ij} = \sum_{ij} \epsilon_{ij} \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^{12} - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right]. \quad (1)$$

$$r_{ij}^0 = \left(\frac{(r_i^0)^6 - (r_j^0)^6}{2} \right)^{\frac{1}{6}}. \quad (2)$$

$$\epsilon_{ij} = 2 \sqrt{\epsilon_i \epsilon_j} \left(\frac{(r_i^0)^3 + (r_j^0)^3}{(r_i^0)^6 + (r_j^0)^6} \right). \quad (3)$$

Waals potential energy summation method are used Ewald&Group and Atom Based respectively. The cut-off radius is 13.5 Å. The equilibration steps are 3,000,000 Monte Carlo moves and the production steps are 3,000,000 Monte Carlo moves. In simulation, the sorption is the function of the fugacity. The gas fugacity in different states is calculated by the PR state equation. Molecular dynamics simulation of low-energy configurations obtained from monte carlo simulation was carried out to obtain the density distribution of the CH₄/CO₂ molecules in the pore. MD simulations are carried out in canonical (NVT) ensemble. Time step is 1.0 fs. Dynamics time is 0.7 ns in which 200ps was used to balance the structure, and 500 ps was used for the statistics of material properties.

Results and discussion

Adsorption capacity with Burial depth. According to the common geothermal gradients (15°C/km) and pressure gradient (30Mpa/km), CH₄ and CO₂ competition adsorption simulated at the burial depth of 1, 2, 3 km. The ratio is set to 4:1, this is because of the smaller amount of CO₂ when it injected into the pore full of CH₄ at the beginning. With the increase of burial depth, temperature and pressure increase simultaneously, so temperature and pressure has a cooperative effects on gas adsorption. In Fig.3, CH₄ sorption increases significantly as burial depth increases, but CO₂ sorption is almost constant. The sorption of CH₄ at 1, 2, 3km. is 8.12, 10.49, 11.32 mmol·cm⁻³ respectively. Sorption of CO₂ at 1, 2, 3km. is 3.47, 3.16, 3.36 mmol·cm⁻³ respectively. The isosteric heat of CH₄ and CO₂ are presented in Fig.4. With the increase of burial depth, the isosteric heat of CH₄ increases successively, and the isosteric heat of CO₂ decreases successively. However, both of them is less than 42 kJ/mol, so the adsorption belongs to physical adsorption.

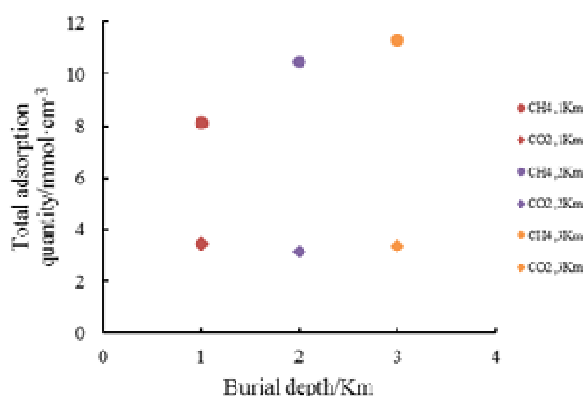


Fig. 3 Total adsorption quantity vs burial depth

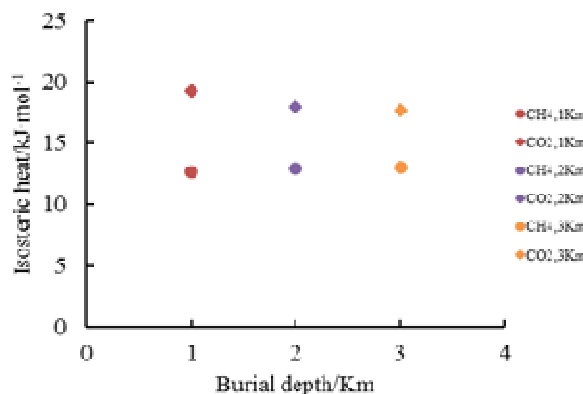


Fig.4 Isosteric heat vs burial depth

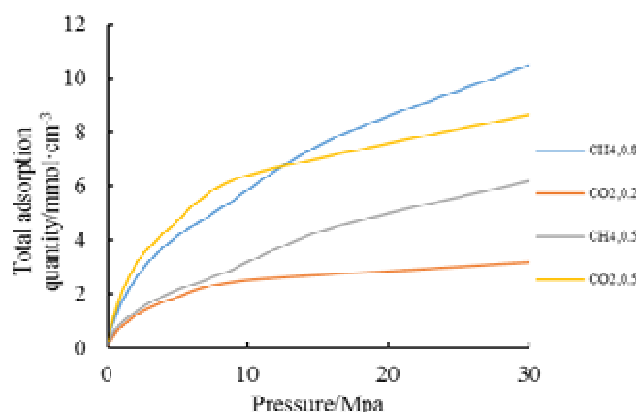


Fig.5. The sorption isotherms of CH₄ and CO₂

Influence of ratio. Fig.5 presents the sorption isotherms of CH₄ and CO₂ with two types of ratio. CH₄ sorption gradient is bigger than CO₂ at low pressure, and the sorption is greater consistently as pressure increases at the ratio of 4:1. On the contrary, CH₄ sorption gradient is smaller than CO₂ at low pressure, and the sorption is smaller within all pressures scope at the ratio of 1:1. Sorption first increase rapidly is due to the gas molecules adsorbed on the surface. In the later, the reason of sorption curve almost linear is that increasing of sorption is dominantly controlled by bulk phase. Isosteric heat of CH₄ and CO₂ are presented in Fig.6. It shows that isosteric heat of CH₄ and CO₂ are in the range of 12.28

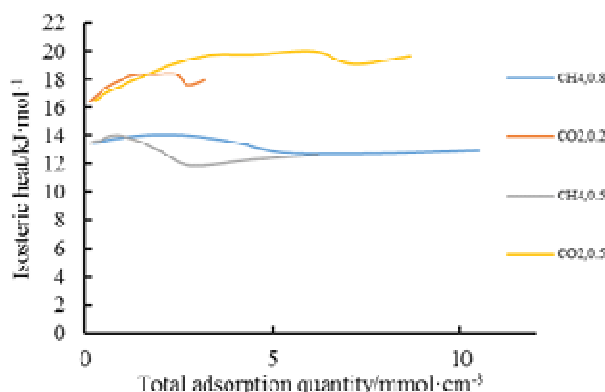


Fig.6 Isosteric heat of CH₄ and CO₂

kJ/mol~13.95 kJ/mol and 16.51 kJ/mol~19.04 kJ/mol respectively. The isosteric heat of adsorption of CO₂ is significantly larger than that of CH₄, which illustrated the strong interaction between CO₂ and graphene slit pores. This is probably due to the fact, that stronger van der Waals and electrostatic gas–gas and gas–adsorbent interactions in the case of CO₂ adsorption [11]. Deformation of the isosteric heat curve with load is first increasing, then the change trend of decrease, and then increase. The reason likely is that, at the beginning of adsorption, the smaller amount adsorbed of gas molecules can increase the adsorption capacity of graphene. Isosteric heat decreases as the loading increases due to the high energy position was gradually occupied. As the adsorption proceeds, isosteric heat increases slightly, because the non-negligible fluid/fluid contribution to the adsorption enthalpy when the pores are filled with CH₄ and CO₂ [6].

Molecular configurations and density. we present the molecular configurations of CH₄/CO₂ molecules at bulk pressure $P = 15.9, 30 \text{ Mpa}$ and temperature $T = 343 \text{ K}$ in organic nanopores with CH₄:CO₂=4:1, 1:1 in Fig.7. In the proximity of surface, the gas molecules have a higher concentration. The proportion of CO₂ on the pore surface is significantly smaller than that of CH₄ in the case of CH₄:CO₂=4:1, while the proportion of CO₂ is larger than that of CH₄ in the case of CH₄:CO₂=1:1. From the figure of molecular configurations we can also observed that orientation of

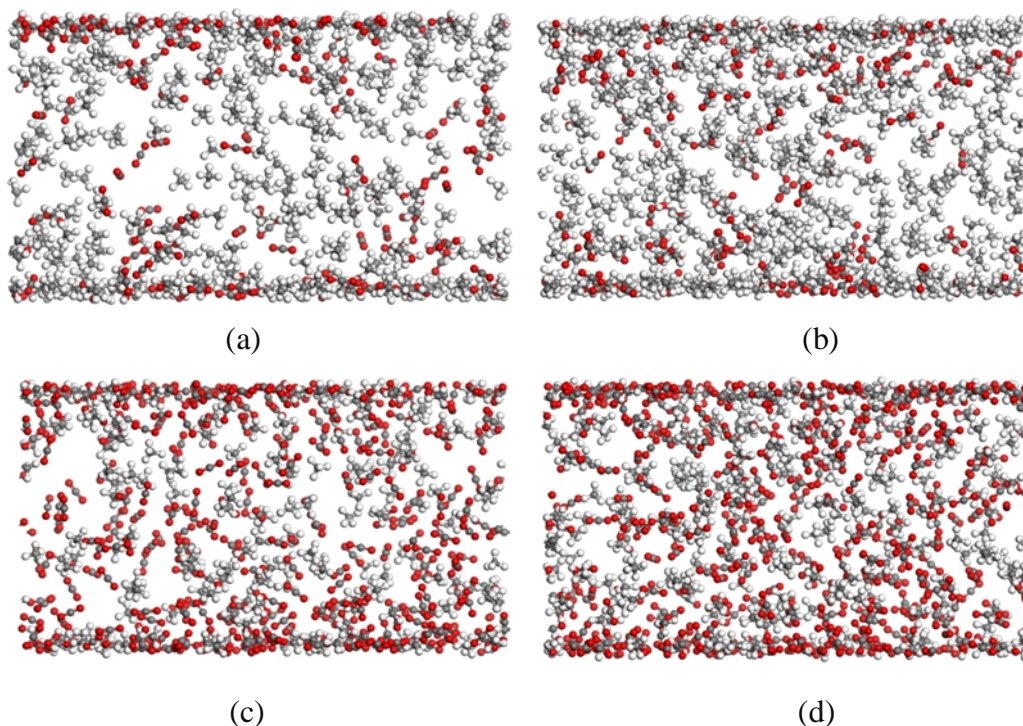


Fig.7 Molecular configurations for CH₄/CO₂ adsorbed at 343 K in a slit carbon nanopore of a width H=3nm, (a) CH₄:CO₂=4:1, 15.9Mpa, (b) CH₄:CO₂=4:1, 30Mpa, (c) CH₄:CO₂=1:1, 15.9 Mpa, (d) CH₄:CO₂=1:1, 30Mpa, The gray spheres are C, the red spheres are O, and white spheres are H. The structure of graphene is omitted.

CO₂ molecules is more parallel in proximity of surfaces. Similar trend has been reported in the study of [12].

To have a better understanding of the adsorption of CH₄/CO₂ molecule in various ratio and pressure, we present density profiles of the adsorbate molecules along the pores in Fig. 10. The height of the graph reflects density of gas molecules at the given position, which can be readily acquired by converting the number of gas molecules at given the volume element that the molecules were divided among. It is clear that the CH₄/CO₂ density profiles is not uniform across the pores, its value is significantly greater near the wall, due to the adsorption, and it decreases as the distance from the pore wall increases. As pressure rises from 15.9 to 30Mpa with CH₄:CO₂=4:1, the density of adsorbed phase increases, but with the greater increases seen in the density of CH₄. Different behavior is observed in the case of CH₄:CO₂=1:1. For CO₂, density is larger than that of CH₄ in the adsorbed phase. However, the quantity of CH₄ is slightly larger than that of CO₂ in the pore central. With increase of pressure the CO₂ has a greater increment of adsorbed phase density relative to CH₄. The ratio of the gas in the pore central is approximately equal to that of the bulk state. This can be attributed that effect of pore wall on gas decreases with increasing distance. In all cases, there are clearly two adsorption layer forming.

In this study, we also calculate the selectivity of graphene for CO₂ relative to CH₄ in CH₄/CO₂ binary mixture for different ratio, as shown in Fig. 8. The selectivity is calculated using the following equation.

$$S_{\text{CO}_2/\text{CH}_4} = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{y_{\text{CO}_2}/y_{\text{CH}_4}} \quad (1)$$

where $S_{\text{CO}_2/\text{CH}_4}$ is the selectivity of component CO₂ relative to CH₄, x_{CO_2} and x_{CH_4} are mole fractions of CH₄ and CO₂ in the adsorbed phase, y_{CO_2} and y_{CH_4} are mole fractions of CH₄ and CO₂ in

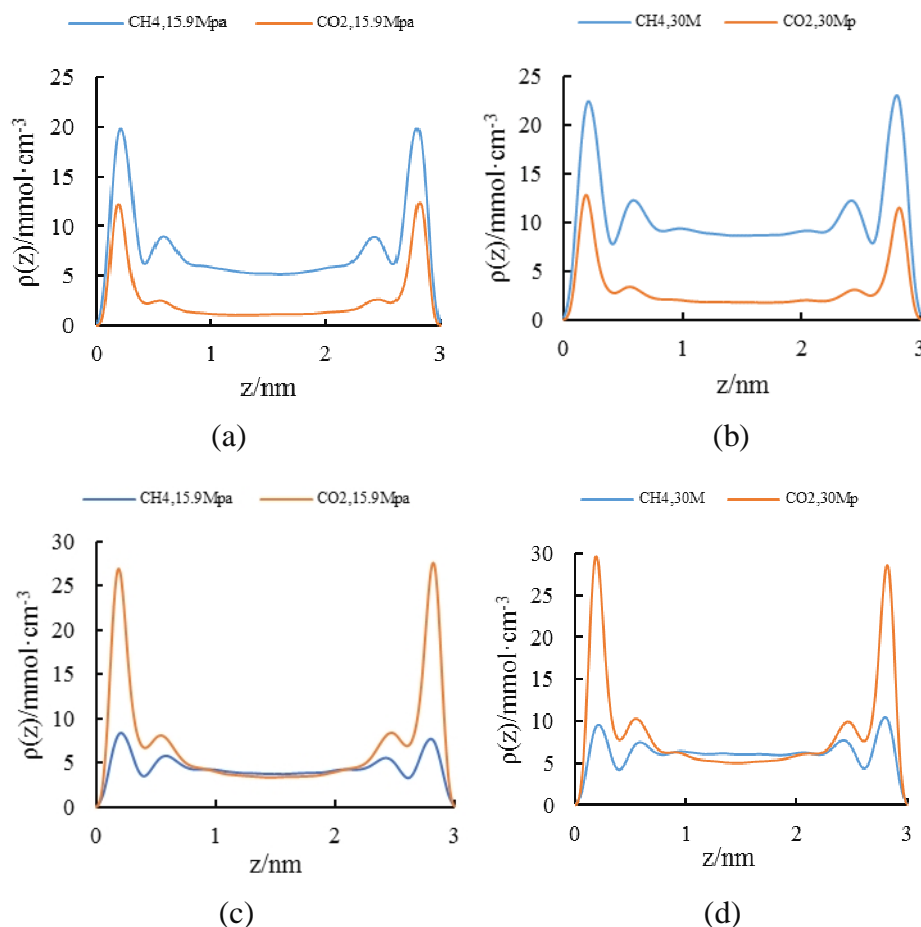


Fig.8 density profiles of the adsorbate molecules along the pore at 343 K in a slit carbon nanopore of a width $H=3\text{nm}$ with
(a) $\text{CH}_4:\text{CO}_2=4:1$, $p=15.9\text{Mpa}$, (b) $\text{CH}_4:\text{CO}_2=4:1$, $p=30\text{Mpa}$, (c) $\text{CH}_4:\text{CO}_2=1:1$, $p=30\text{Mpa}$, (d) $\text{CH}_4:\text{CO}_2=1:1$, $p=30\text{Mpa}$.

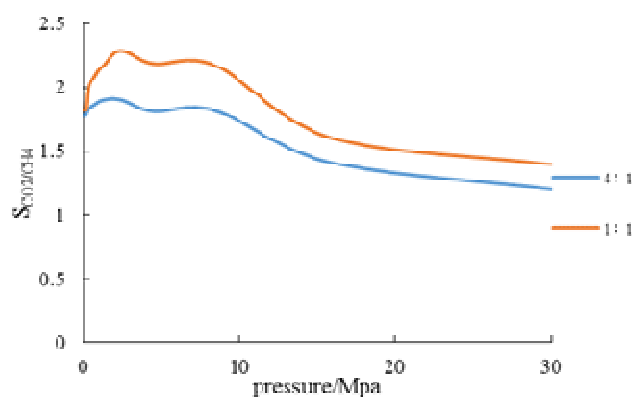


Fig.9 Selectivity of graphene with $\text{CH}_4:\text{CO}_2=4:1$ and $1:1$ for CO_2 relative to CH_4

the bulk phase. Fig.8 shows that selectivity coefficient increases with the increase of pressure firstly and followed by a subsequent decrease, which suggests that adsorption capacity of CO_2 strengthened first and then weakened. In addition, the increase in the CO_2 ratio strengthens its adsorption capacity. Both selectivity coefficient with different proportion are close to 1 finally. This is mainly because that gas molecular in the bulk phase is dominated in the pore at the high pressure.

Conclusions

This paper investigated the competitive adsorption law of CH_4 and CO_2 via Molecular simulation method. We used GCMC simulations and studied the sorption of CH_4 and CO_2 . The sorption of CH_4 increases clearly as burial depth increases, but sorption of CO_2 is almost constant. CH_4 sorption is larger than that of CO_2 with the $\text{CH}_4:\text{CO}_2=4:1$, while CH_4 sorption is smaller than that of CO_2 in the case of $\text{CH}_4:\text{CO}_2=1:1$. Moreover CO_2 has a larger isosteric heat that suggested stronger adsorption capacity of CO_2 .

We then used molecular dynamics methods to study the density profiles and molecular configurations of the CH_4/CO_2 binary mixture gas. We observed that orientation of CO_2 molecules is more parallel in proximity of graphene surfaces, and found that CO_2 sorption in proximity of surfaces is significantly larger than that of CH_4 in the case of $\text{CH}_4:\text{CO}_2=1:1$. The ratio of the gas in the pore central is approximately equal to that of the bulk state.

Selectivity of graphene for CO_2 relative to CH_4 reveal that the higher CO_2 ratio, the stronger CO_2 adsorption capacity.

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