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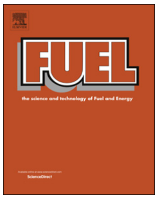

Full Length Article

GCMC simulations on the adsorption mechanisms of CH_4 and CO_2 in K-illite and their implications for shale gas exploration and development

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ABSTRACT

Understanding the adsorption mechanism of shale gas is an essential pre-requisite for establishing models to evaluate the adsorbed gas amount under geological conditions quantitatively and to guide shale gas exploration and development. By using the Grand Canonical Monte Carlo (GCMC) method, we simulated the adsorption behavior of CH_4 and CO_2 in K-illite slit pores, and revealed the key gas adsorption mechanisms and discussed their implications on shale gas exploration and development by analyzing the distribution of gas mole concentration, gas-surface interaction energy, density field and etc. It is found that even with the presence of weak adsorption layers in meso and macro pores, the adsorption behavior of both CH_4 and CO_2 is dominated by the strong adsorption layers and thus can only be approximated but not strictly described by the classic Langmuir model. However, the micro-pore filling effect leads to the overlap of adsorption layers in micro pores, causing more deviation when using the classic Langmuir model to evaluate the adsorption behavior. Even though the adsorption behavior is not affected by pore size dimensions in meso and macro pores, the proportion of the adsorbed gas increases with the decreasing pore size. Both CH_4 and CO_2 are adsorbed in the center of the six-membered oxygen ring on the silicon oxygen tetrahedron surface. The CH_4 molecules (with no polarity) are at the center of the ring, but the CO_2 molecules (with electric quadrupole moment) are closer to the oxygen atom with polarity in the ring. The electric quadrupole moment makes the adsorption capacity of CO_2 much stronger than that of CH_4 in K-illite pores, providing a theoretical basis for enhancing CH_4 recovery efficiency by injecting CO_2 in the development of shale gas.

1. Introduction

Recent exploration and development show that shale gas is the greatest potential resource among the unconventional oil and gas resources [1]. In shale reservoir, gas exists in the forms of adsorbed gas, free gas and the soluble gas in both formation water and organic matters, with the adsorbed gas accounting for 20–80% of the total gas amount [2]. Understanding the adsorption mechanism of shale gas can provide a theoretical basis for evaluating the adsorbed gas amount quantitatively, which is of great importance to both shale gas resource assessment and development.

Previously, the adsorption behavior of gases was primarily investigated by using adsorption experiments [3–6]. As adsorption experiments can only provide the excess adsorption amount, they do not provide the full insight on the adsorption mechanisms. Grand Canonical Monte Carlo (GCMC) simulations can provide both the excess and absolute adsorption amounts, and also some essential parameters (e.g., gas mole concentration distribution, gas-surface interaction energy distribution, density field and etc.) that can reflect the connotation of the adsorption behavior of gases in shale, and thus offers additional information on the shale gas adsorption mechanisms [7–17].

Although the GCMC method was used in previous studies to reveal

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shale gas adsorption mechanisms, there are still some outstanding issues. For example, the average interaction energy between all molecules in pores and the mineral surface was usually used to characterize the adsorption strength between gas and mineral surface [13–15,17,18]. However, when the pore sizes are large enough, the gas molecules in the center of the mineral pores may be beyond the interaction scope from the mineral surfaces. This will downgrade the average interaction energy. Therefore, the average interaction energy cannot be adequately used to accurately reflect the adsorption strength, especially when investigating the adsorption behavior in pores with varying sizes. The second example is that the radial distribution function (RDF) was conventionally used to determine the adsorption site in previous investigations on shale gas by using the GCMC method [11–13,19]. RDF can only reflect the distribution characteristics between atoms, while not all the adsorption sites are just on the atom. Therefore, RDF is not a suitable parameter to investigate adsorption sites. Without proper parameters to reflect the gas-surface interaction strength or to reflect the adsorption sites, the adsorption mechanisms of gases in shales cannot be correctly understood.

To address these problems, we used illite, a common clay mineral that has the highest abundance in the gas-bearing shale in China, to investigate the adsorption behavior of CH_4 and CO_2 in slit pores by using GCMC simulations. We attempted to compute the interaction energy at varying locations in the pore to obtain the interaction energy distribution curves, the mole concentration distribution curves and the density field maps of gas, and further investigate the adsorption layer, adsorption site and the pore size effects on the adsorption behaviors. The primary purposes of this paper are to understand the shale gas adsorption mechanisms in K-illite slit pores, to further discuss the proportion of the adsorbed gas, the validity of adsorption model and the enhancement of the recovery of CH_4 by injecting CO_2 theoretically, so as to provide insight for exploration and development.

2. Methods

2.1. Models

In the adsorption system, the adsorbent is K-illite, whose proportion is the highest among clay minerals in gas-bearing shales in China, especially in Yangtze region [20], and the adsorbates are CH_4 and CO_2, respectively.

The K-illite is represented by dioctahedral illite with the general unit cell formula of $K_x[Si_aAl_{8-a}][Al_bMg_{4-b}]O_{20}(OH)_4$ [21], and the lattice parameters (Table 1) and the atomic positions (Table 2) are shown below. According to the isomorphic substitution in natural K-illite, we substituted 3 Si^{4+} by Al^{3+} every 16 Si^{4+} in the tetrahedral sheet, and substituted 3 Al^{3+} by Mg^{2+} every 40 Al^{3+} in the octahedral sheet. The negative charges caused by the substitution was balanced by the interlayer K^+ [22], forming a unit cell formula of $K_{1.8}[Si_{6.5}Al_{1.5}][Al_{3.7}Mg_{0.3}]O_{20}(OH)_4$ [23].

The simulation cell consists of two illite layers and the pore space in between, forming a slit pore (Fig. 1). Because the impact of pore wall thickness on adsorption behavior is negligible [15,17], we set the pore wall thickness as thin as possible (half layer of illite sheet) in order to simplify the simulation, and to keep consistency with the previous study [16]. The potassium cations and gas molecules are filled in the slit pore (Fig. 1). Three-dimensional periodic boundary conditions were applied to the simulation cell, which consists of 24 (6 × 4 × 1) unit cell, making the size in the x- and y-dimension 3.11 nm and 3.56 nm, respectively. We define the pore size (H) as the distance between two inner surfaces of the pore walls formed by oxygen atoms in silicon tetrahedron (Fig. 1). To investigate the impact of pore size on the adsorption behavior, we set the pore size as 0.75 nm, 1 nm, 1.5 nm, 2 nm, 4 nm, 6 nm and 8 nm, respectively. In the simulations, the cutoff radius is set to be 1.25 nm. To ensure the size of the simulation cell in the z direction is over twice of the cutoff radius (2.5 nm), we repeated the simulation cell in the z dimension if its size is smaller than 2.5 nm (in the cases of pore sizes less than 1.5 nm). The interactions among atoms in K-illite are described by CLAYFF [24], with potassium cations being fixed on the mineral surface.

Table 1
Lattice parameters of RM30 illite.

Edge length (Å)		Internal angles (°)	
a	5.2021	α	90
b	8.9797	β	101.57
c	10.226	γ	90

Table 2
Atomic positions of the illite in unit cell.

Atom	x	y	z
K	0	0.5	0.5
Al	0.5	0.1667	0
Si	0.4191	0.328	0.2688
O1	0.3487	0.31	0.1063
O2	0.4984	0.5	0.3131
O3	0.6715	0.2246	0.335
OH	0.4191	0	0.1006

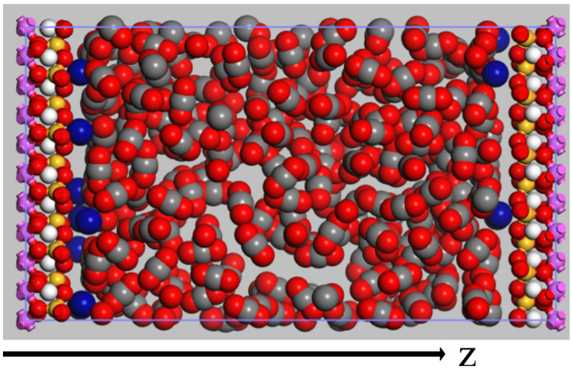

Fig. 1. A snapshot of K-illite simulation cell with methane, carbon dioxide molecules and potassium cations in between. Gas molecules and potassium cations are represented by spheres while clay layers are represented by ball-stick structures, with the color scheme: O, red; H, white; Si, yellow; Al, pink; K, blue; C, grey; united CH_4, orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We used the TraPPE force field [25,26] to describe the interactions between atoms in CH_4 and CO_2 molecules. To simplify the simulation, the C atom together with H atoms bond to it in a CH_4 molecule are treated as a united atom [25]. For a CO_2 molecule, the O–C bond length and O–C–O bond angle are determined by the experimental measurements, which are 1.16 Å and 180° [27], respectively, and the charge on the C and O sites are $+0.7\,e$ and $-0.35\,e$, respectively. The force field parameters for both the illite (CLAYFF) and the gas molecules (TraPPE) are shown in Table 3.

In the simulation system, the adsorption behavior is determined by both gas-surface and gas-gas interactions, which are dominated by both Van der Waals force and Coulomb force. We describe the Van der Waals force between particles by using Lennard-Jones 12-6 potential [28]:

$$E(r_{ij}) = \begin{cases} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] & for\ (r_{ij} \leqslant r_{cutoff}) \\ 0 & for\ (r_{ij} \geqslant r_{cutoff}) \end{cases}, \quad (1)$$

where the separation between the atom *i* and *j* is represented by r_{ij}, and the well depth of *LJ* potential and the *LJ* radius are represented by ε_{ij} and σ_{ij}, respectively. The cutoff radius is r_{cutoff} with the value of