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Molecular simulation of adsorption behaviors of methane, carbon dioxide and their mixtures on kerogen: Effect of kerogen maturity and moisture content

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ABSTRACT

The adsorption behaviors of methane (CH_4), carbon dioxide (CO_2) and their mixtures are vital to understand the process of CO_2 sequestration and shale gas exploitation. In this work, four realistic kerogen models with different maturities (immature (IIA), beginning of oil window (IIB), middle of oil window (IIC), postmature (IID)) were built by the molecular dynamics (MD) method. The adsorption characteristics of CH_4, CO_2 and their mixtures on these kerogen models with various moisture contents (0, 0.7, 1.4, 2.1, 2.8 wt%) were investigated by the grand canonical Monte Carlo (GCMC) simulations. The influences of kerogen maturity and moisture content on the adsorption capacity, isosteric heat of adsorption and adsorption selectivity of gas molecules were discussed. Simulation results show that the maximum adsorption capacity of gas molecules increases with increasing kerogen maturity, but decreases with increasing moisture content, and the reduction decreases as the maturity increases at high moisture contents. The average isosteric heat of CO_2 adsorption is relevant to the sulfur/oxygen content of kerogen models. The pre-adsorbed water (H_2O) has a small effect on the gas isosteric adsorption heat when located in the middle of pores, but can reduce the CO_2 isosteric adsorption heat by occupying the hydrophilic groups. Moreover, H_2O molecules are observed to migrate and aggregate into growing clusters at higher moisture contents for kerogen IIC and IID models, increasing the gas isosteric adsorption heat. The CO_2/CH_4 adsorption selectivity gradually decreases to the equilibrium value with the rise of bulk pressure. Also, the selectivity decreases with increasing CO_2 mole fraction for lower mature kerogen models (IIA and IIB), but increases with the CO_2 mole fraction at low pressure for kerogen models of higher maturity (IIC and IID). Meanwhile, the selectivity increases for IIA, IIC and IID models, while decreases for IIB model as the moisture content increases. This study gains deep insights into the effect of kerogen maturity and moisture content on the interaction between CH_4/CO_2 and kerogen at microscopic scale.

1. Introduction

As one of the most promising alternatives to conventional gas resources, shale gas has attracted enormous attentions worldwide for its considerable abundance and high utilization efficiency [1,2]. However, the tight shale reservoir and the complex gas transport mechanisms, along with the natural depletion development regime, result in a low recovery of shale gas reservoirs. Thus the enhancement of gas recovery becomes the key topic for the development of shale gas reservoirs. Injection of CO_2 into coal seams has been proved to be one effective strategy for recovery enhancement of coalbed methane as well as CO_2 sequestration in the past decades [3–5]. This strategy has recently received increasing attentions as one potential technique for CO_2 storage with the potential for enhanced shale gas recovery [6–8]. To further understand this process, a detailed understanding of the adsorption characteristics of shale with CH_4, CO_2 and their mixtures is essential.

The adsorption characteristics of organic matter under reservoir conditions are associated with many factors such as the total carbon content (TOC), kerogen type and maturity, surface functional group, as well as the temperature and moisture content [9]. Of these factors, moisture content acts as one of the most key roles in gas adsorption [10–12]. Clay mineral in shale is widely accepted as water-wet, while

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organic matter is traditionally assumed as hydrocarbon-wet [13]. However, experimental and simulation work recently found that kerogen is actually mixed-wet due to the hydrophilic characteristic of oxygen-bearing groups [14]. Shale in the reservoir is originally at moisture equilibrated conditions [15]. H_2O molecules can not only block the throats of shale, but also occupy the adsorption sites for gas molecules, thus rapidly reducing the adsorption capacity [16–17]. Another significant parameter relevant to gas adsorption is the maturity of organic matter in shale. Almost half of the total hydrocarbons in shale are adsorbed in the organic matter for its abundant adsorption sites [18]. The organic matter maturity is closely correlated with the surface functional groups and micropore volumes, which directly determine the gas adsorption capacity [19]. Therefore, the influence of moisture content and maturity on adsorption characteristics of shale should be emphasized and discussed in detail.

To date, some experimental attempts have been made to investigate the adsorption characteristics of organic materials considering the influence of maturity and moisture content. Gas adsorption capacity has been observed to be reduced significantly with the equilibrated moisture in shale and coal [19,20]. Meanwhile, adsorption capacity of shale gas has been found to be linearly correlated with the maturity [21–23]. Particularly, it increases as the maturity increases [21]. Gensterblum et al. [10] experimentally investigated the competitive adsorption of CH_4 and CO_2 on organic material in the presence of moisture. Gensterblum et al. [24] studied the effect of coal rank and moisture content on CH_4 and CO_2 adsorption on natural coals. Experimental investigation is the fundamental method for understanding gas adsorption process [25]. Also, experimental data are important reference resources for evaluating the validity of molecular models. The development of molecular simulation provides an effective tool for predicting adsorption performances of gas molecules in complex systems at molecular scale [26,27], which is complemental to the experimental study. Encouraging results for studies on gas adsorption behaviors with molecular simulation techniques have been reported [27–29]. Zhang et al. [27] investigated the adsorption characteristics of CH_4 on dry and moist coal with the combined Monte Carlo and MD simulations. Liu et al. [28] studied the influence of moisture content on the adsorption behaviors of pure CH_4, CO_2, N_2 molecules and their mixed gases on coal models with heterogeneous surface through GCMC simulations. Zhao et al. [29] used GCMC simulations to discuss the effect of kerogen maturity and moisture content on CH_4 adsorption capacity and adsorption heat on type II kerogens. However, it should be noted that since actual kerogens are complex and heterogeneous macromolecules, the present average structures used as models are difficult to capture all of the structure details. Although many efforts have be made to involve important kerogen structure details and improve the rationality of kerogen molecular structures, it is essential to validate these structures by comparing simulated adsorption isotherms with experimental data before analyzing gas adsorption mechanism. Moreover, in addition to kerogen component, mineral component of shale also contributes to the overall adsorption capacity. Unfortunately, representative shale molecular models involving both kerogen and mineral components remain to be developed and improved. So far, gas adsorption behaviors on kerogen and mineral components are mainly separated investigated for the molecular simulation studies in the literature. Although many efforts have been devoted to understanding the effect of maturity and moisture content on gas adsorption capacity, to our best knowledge, the microscopic adsorption mechanisms of pure CH_4, CO_2 and their binary mixtures on different mature kerogens with the presence of various moisture contents have not been investigated so far, and our work aims to gain insights into this topic.

In this work, we focused on the type II kerogen from the organic-rich shale formation [30]. Four different mature kerogen units from the work of Ungerer et al. [31] were selected to develop the bulk kerogen models through the MD method. Based on these realistic kerogen models, the adsorption behaviors of pure CH_4, CO_2 and their binary mixtures associated with various moisture contents (0, 0.7, 1.4, 2.1, 2.8 wt%) were investigated by GCMC simulations. The influences of kerogen maturity and moisture content on the adsorption capacity, isosteric heat of adsorption and adsorption selectivity of gas molecules were discussed. To quantify the effect on adsorption capacity, the pore structural parameters of kerogen models of different maturities and moisture contents were calculated. The radial distribution function (RDF) was computed to analyze the affinity between CH_4/CO_2 molecules with atoms in the kerogen model. In the case of moisture effect on the isosteric heat of adsorption, the distributions of H_2O molecules in different mature kerogen models were visualized. This study is hoped to gain insights into the influence mechanisms of maturity and moisture content on adsorption behaviors of CH_4, CO_2 and their mixtures on kerogen and to provide theoretic guide for the project of enhanced shale gas recovery by CO_2 sequestration.

2. Computational methodology

2.1. Kerogen structure units

The structure units of kerogen models (Fig. A.1) adopted in this work were built by Ungerer et al. [31] referring to the analytical experimental data from the work of IFP-EN and Exxon researchers [32]. The four kerogen units correspond to the organic-rich marine shales from the Duvernay series at an increasing maturity from immature to postmature. The type II kerogen is not only typical source of conventional oil and gas resources, such as these in the North Sea and western Canada [31]. The mature kerogen IIC is representative of organic matter in unconventional liquid hydrocarbons reservoirs, similar to that in the Bakken shale [33,34], while the postmature kerogen IID is associated with organic matter in unconventional gas formations such as the Barnett shale [35]. The detailed structural and compositional parameters of these kerogen units can be found in the work of Ungerer et al. [31], which match fairly well with the results of analytical experiments including the solid-state C^{13} NMR spectroscopy and X-ray techniques [32].

2.2. Molecular models of bulk kerogen

The condensed bulk kerogen models are generated through a combination of geometry optimization and MD simulations in Materials Studio using COMPASS force field [36]. This all-atom force field adopts the molecular potential of Lennard-Jones 6–9 to describe the dispersion-repulsion interactions between atomic pairs. It is widely used for its high accuracy in thermodynamic properties prediction for both organic and inorganic compounds in condensed phase [37].

Initially, the structures of kerogen units are relaxed by geometry optimization and annealing simulations [38]. We adopt the smart minimization algorithm with a fine convergence criterion to optimize the structure geometry. The non-bonded interactions including Coulomb and Van der Waals are calculated based on atom [38], and a fine cutoff distance of 15.5 Å is adopted. For the annealing method, 10 annealing cycles with increasing temperature from 300 to 800 K are selected. The simulations are carried out with the canonical ensemble (NVT) [37], in which the molecular number, box volume and system temperature are fixed, and a total simulation time of 400 ps is executed to bring the structures to the lowest energy state.

Thereafter, 6–12 optimized kerogen units are enclosed in a big simulation box with periodic boundary conditions to generate the initial configurations of kerogen models, with the target density being 0.1 g/cm^3 [29,31,34]. The number of kerogen units for each kerogen model is determined to guarantee similar system size and computational