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Combined Monte Carlo and molecular dynamics simulation of methane adsorption on dry and moist coal

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HIGHLIGHTS

- Combined MD and MC methods was first used to address coal swelling.
- Temperature has no effect on the maximum adsorption expressed on a volume basis.
- Quantify CH_4 absorption for both dry and moist coal.
- Effect of water on CH_4 adsorption and coal swelling mechanism were investigated.
- Water is preferably adsorbed on oxygen and nitrogen atoms.

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ABSTRACT

A quantitative understanding of methane (CH_4) adsorption on dry and moist coal and the mechanism of coal swelling is vital for successful coal bed methane (CBM) projects. CH_4 adsorption isotherms of coal with moisture contents ranging from 0 to 3 wt% water, the temperature effect on maximum adsorption capacity, coal swelling, and adsorbed phase density have been modeled by performing combined Monte Carlo (MC) and molecular dynamics (MD) simulations at temperatures of 308 and 370 K (35 and 97 °C) and at pressures up to 10 MPa. Simulation results demonstrate that absolute adsorption (expressed as a mass basis) divided by bulk density is independent of temperature for CH_4 on dry coal when pressure is over 8 MPa. Both the adsorption capacity and adsorption rate of CH_4 decrease, while coal swells as moisture content increases. These results show that the presence of water in the coal matrix reduces the interaction between the coal and methane. Our results indicate that coal–water interaction dominates and is the main contributing factor to the coal swelling. The interaction of CH_4–H_2O and CH_4–CH_4 is negligible and the absolute adsorption of CH_4 on both dry and moist coal follows the Langmuir isotherm for the pressure range simulated. This study provides a quantitative understanding of the effects of moisture and temperature on CH_4 adsorption, coal swelling, and the adsorbed CH_4 density from a microscopic perspective. Molecular modeling proves to be a valuable and cost-effective tool for studying gas adsorption behavior in complex and complicated systems.

1. Introduction

Coal bed methane (CBM) is an alternative and generally lower risk source of unconventional gas and it could provide an alternative source of cleaner energy in global markets for years to come. Furthermore, unmineable coal beds are potential candidates for carbon dioxide (CO_2) storage with the potential for enhanced coal-bed methane recovery (ECBM). To understand ECBM processes, gas interaction with coal via adsorption is a key aspect. Moreover, a unique phenomenon is coal swelling induced by gas adsorption, which has a great impact on coal reservoir permeability change and thus is important for gas flow and well productivity/injectivity. Adsorption of gases in coals has been studied experimentally for decades. Goodman et al. [1] investigated the inter-laboratory reproducibility of CO_2 isotherm measurements on moisture-equilibrated coal samples and found agreement among the laboratories was good up to 8 MPa. At higher pressures, the results among the laboratories diverged significantly. The adsorption capacity of gas in coal is known to be affected by many factors such as the maturity (coal rank), organofacies (i.e. content of macerals especially vitrinite%), ash content, porosity, heterogeneity of the surface functional groups of the coal and as well as prevailing conditions of pressure, temperature and water content [2]. Mosher et al. [3]

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characterized the effect of pore size on methane adsorption in micro and mesoporous carbon-based systems. Liu and Wilcox investigated the influence of realistic surface functional groups of carbon pore surfaces on the adsorption of pure CO_2 [4–6] and gas mixtures [7] by performing plane-wave electronic structure calculations. Billemont et al. [8] reported both experiments and molecular simulations on the adsorption of CO_2 and CH_4 in porous carbons in the presence of water. Gensterblum et al. [9] experimentally showed the evidence of competitive adsorption of H_2O, CO_2 and CH_4 on organic material. Gensterblum et al. [2,10] studied CO_2 and CH_4 sorption on natural coals and its dependence on coal specific parameters like coal rank, maceral composition or ash content and moisture. Pan et al. [11–13] described adsorption-induced coal swelling and how adsorption capacity and permeability are affected.

Molecular simulations play an important role in the determination of various properties of complex and complicated systems without any assumptions, such as absolute adsorption capacity, including under some extreme conditions, where experiments are impractical or impossible. Some molecular simulations have been carried out on the adsorption and confinement of gas in porous carbon [14–19]. Recently, Brochard et al. [20] have successfully applied molecular simulation to investigate the competitive adsorption behavior of different gases. However, in their CS1000 coal model, oxygen atoms are not accounted for, whereas in natural coal, oxygen amounts up to 10% of the total mass and oxygen atoms significantly influence the distribution of charge. Therefore, this model is not accurate in the presence of water. Liquid water is commonly present in coal seams and is known to affect the gas production rates, CO_2 interactions and coal swelling [21,22]. Therefore, for field applications, the effect of water cannot be ignored. Billemont et al. [8] have performed molecular simulations in porous carbons without taking complex pore shape, morphological disorder and the swelling effect into account. Tambach et al. [23] and Hu et al. [24] have investigated the diffusion and sorption behavior of CH_4 and CO_2 in coal. However, coal swelling was not considered in those works.

In this paper, we report combined MC and MD simulations on the adsorption of CH_4 in dry and moist coals over a pressure range of 0.1–10 MPa. In the case of dry coal, two temperatures of 308 and 370 K (35 and 97 °C) are considered to examine the temperature effect. For the moist coals, two pre-adsorbed water contents of 1.2 wt% and 3.0 wt% are simulated at 308 K. Molecular simulations consist of determining the absolute and excess adsorption isotherms, interaction energy, isosteric heat of adsorption, coal swelling, adsorbed phase density, radial distribution functions between the surface functional groups and CH_4 and the diffusion coefficient. The objectives of this work were to better understand CH_4/water/coal interactions and shed light on the details of the effect of water on the adsorption capacity, coal swelling and transport properties of CH_4 in coal matrix at the atomic level, as well as to demonstrate the potential use of this modeling method for CBM. The method consists of switching the MD trajectory calculations in the constant pressure and temperature ensemble to the MC simulations performed in the Grand Canonical statistical ensemble, in which the chemical potential of the CH_4, the volume, and the temperature of the system are fixed. Further details are given in Section 2.

The remainder of this article is structured as follows. In Section 2 we explain the molecular models selected for coal, CH_4, water, the methods used, and the implementation of the simulations. In Section 3 we present and discuss the results of the adsorption simulations of the CH_4 in dry and moist coal with 1.2 and 3.0 wt% water. Finally we summarize our analysis and draw conclusions in Section 4.

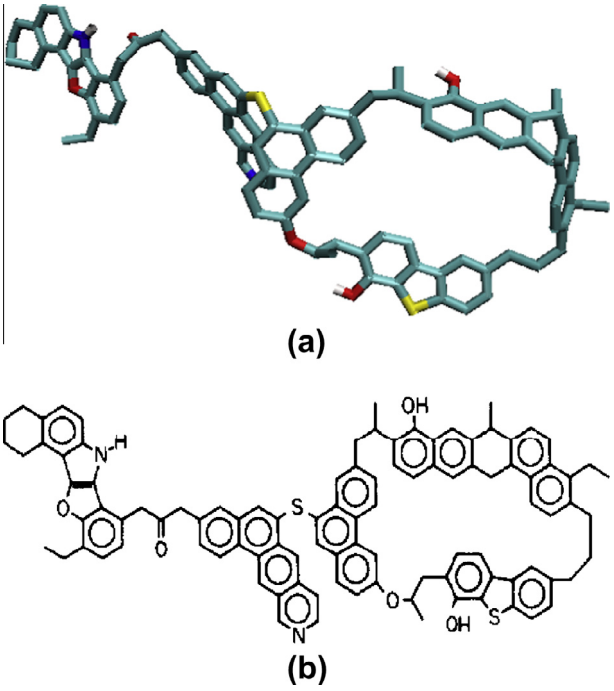

Fig. 1. Building block of intermediate rank coal. (a) Model structure; (b) chemical structure.

2. Simulation details

2.1. Molecular model for coal, water, and CH_4

The formation of coal from a variety of plant materials via biochemical and geochemical processes is called coalification. The nature of the constituents in coal is related to the degree of coalification, termed rank. Increasing rank is accompanied by a rise in the carbon and energy contents and a decrease in the moisture, oxygen and hydrogen content of the coal. A large number (more than 125) of molecular representations for coals have been proposed in the literature that span the entire rank range from brown coal to anthracite. While advancements in computational power and software development have been important, it is the generation of realistic molecular models of coal that have been the most significant barrier to using these models to solve practical problems in coal related projects [25]. The main constituent of coal is carbon atoms which represent about 80% of the total mass of coal on a dry ash-free basis [26]. Apart from carbon, oxygen, hydrogen, nitrogen, and sulfur are constituent elements. In this study, we focus on a model representation of a bituminous coal [23,27]. The development of the molecular coal model started with an intermediate-rank bituminous coal building block ($C_{100}H_{82}O_5N_2S_2$) of 191 atoms, shown in Fig. 1. This building block exhibits an amorphous molecular structure with an aromatic skeleton. Our preferred molecular representation of coal consists of 12 building blocks in the periodic box (see Fig. 2). It was constructed by using Prodrg server [28]. In this model, carbon, hydrogen, oxygen, nitrogen, and sulfur cover about 82.53%, 5.64%, 5.5%, 1.93% and 4.4% of the total mass of the coal, respectively. The contents of oxygen and hydrogen are the most significant after the content of carbon, since oxygen and hydrogen each constitute more than 5% of the total mass of coal. Constituents and their ratios in this model are similar to that observed in natural bituminous coal and they account for the amorphous and chemically heterogeneous structure of the natural coal. As the modeled coal molecule accounts for the presence of oxygen and hydrogen atoms, this makes it more suitable to re-