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Full Length Article

Adsorption of methane in organic-rich shale nanopores: An experimental and molecular simulation study

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HIGHLIGHTS

- The proportion of adsorbed gas decreased as pressure increases under the same pore size and decreased as pore size increases under the same pressure.
- The methane was mainly in free state under higher pressure in different types of pores when the pore size was more than 6 nm.
- The methane adsorption capacity in different types of pores decreased in the following order: organic pore > clay minerals pore > quartz pore.
- The organic pores contributed more to the adsorbed gas while the quartz pores contributed more to the free gas.

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ABSTRACT

In this article, the adsorption behaviors of methane on organic-rich shales were investigated through experimental and molecular simulation. The results showed that the methane adsorption capacity on kerogen is much greater than that of minerals and the methane adsorption capacity of clay minerals is greater than that on quartz. The isosteric heats of adsorption of methane decrease upon increasing the pore size or decreasing the O/C ratio. The volume proportion of adsorbed gas decreases as the pressure increases under the same pore size and declines as the pore size increases under the same pressure. The methane is mainly in the free state under high pressure in different types of pores of organic-rich shales when the pore size is greater than 6 nm. The organic pores contribute more to the adsorbed gas, whereas the quartz pores contribute more to the free gas. The methane adsorption capacity decreases in the following order: organic pore > clay mineral pore > quartz pore. The methane adsorption capacity in the micropores increases with the increasing pore size, whereas that in the mesopores decreases. The methane adsorption capacity under the same pore size decreases with the decreasing O/C ratio. There are differences in the methane adsorption capacity on clay minerals between the macroscopic level and microscopic level, which probably refers to the specific surface. With an increasing pressure or decreasing pore size, the adsorption sites of methane in different types of pores gradually change from higher-energy adsorption sites to lower ones, resulting in an increase in the methane adsorption capacity.

1. Introduction

With the increasing global demand for energy and the improvement of advanced techniques, unconventional oil and gas reservoirs have gradually become the focus of exploration and development in the United States and many other countries, such as Canada, China and Europe [1]. In 2013, the EIA reported that the global technically recoverable reserves of shale gas was 220.73×10^{12} m^3 [2], indicating the abundance of the resource and its great potential for production. The main modes of occurrence of the shale gas include the free state, the adsorbed state and the dissolved state [3]. On the basis of investigating the reservoir characteristics of the shale gas reservoirs in the U.S.A, Curtis [4] suggested that the volume proportion of the adsorbed gas ranged from 20% to 85%, indicating that it makes up a sizeable share of the total shale gas. Therefore, it is significant to investigate the methane adsorption capacity on organic-rich shales for shale gas resource evaluation. In addition to the environmental factors, such as the pressure and the temperature, and the moisture content and purity of the methane, the physical and chemical properties (e.g.,

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organic matter and mineral composition) of the shales can also significantly impact the methane adsorption capacity. In previous studies [5–8], we showed that the compositions of the organic-rich shales from the Yanchang Formation in the Ordos Basin and the Longmaxi Formation and Wufeng Formation of the Sichuan Basin were divided into organic matter (kerogen) and inorganic matter (mineral components). The inorganic matter is composed of non-clay minerals (quartz, feldspars, carbonates) and clay minerals (illite, illite/smectite and chlorite). The methane adsorption capacities of the organic matter and mineral components are thus important for evaluating the methane adsorption capacity on shales.

Recently, isothermal adsorption experiments were conducted, mainly aimed at investigating the methane adsorption capacity on organic-rich shales. Much research has been carried out to evaluate the methane adsorption capacity on pure minerals, such as quartz, montmorillonite, illite, kaolinite and chlorite. Lu et al. [9], Cheng and Huang [10], Ross and Bustin [11], Ji et al. [12–15], Liu et al. [16], Fan et al. [17], Heller et al. [18] and Liang et al. [19] investigated the methane adsorption capacity on clay-rich rocks, pure clay minerals (montmorillonite, illite, kaolinite and chlorite) or pure quartz using isothermal adsorption experiments and discussed the influence factors, including the temperature, pressure, and sample size. Other researchers studied the methane adsorption capacity on kerogen isolated from organic-rich shales. Liang et al. [19], Zhang et al. [20] and Rexer et al. [21] studied the methane adsorption capacity on different types of kerogen isolated from different shales and discussed the influence factors, including the temperature, pressure, and water content. Still other researchers carried out isothermal adsorption experiments targeted at determining the methane adsorption capacity of shales. Chalmers et al. [22,23], Ross et al. [24], Rexer et al. [25], Hou et al. [26], Zhou et al. [27], Gasparik et al. [28] and Yang et al. [29] conducted isothermal adsorption experiments on organic-rich shales from different formations to examine the methane adsorption capacity and discussed the influences of the temperature, pressure and water content. These researchers studied the influences of the clay minerals and TOC content on the methane adsorption capacity using statistical methods. All of these studies contrasted and compared the methane adsorption capacity on clay minerals, quartz, kerogen and organic-rich shales using the Langmuir parameters under equilibrium conditions, which were regarded as the results of the macroscopic adsorption behaviors. According to the previous studies [9–19], the order of the methane adsorption capacities on the different types of clay minerals had not yet been definitively determined, that is to say, different scholars obtained different results. This indicates that the adsorbed amount obtained from isothermal adsorption experiments only reflects the specific surface area of the clay minerals and the adsorption amount per unit surface area, rather than intrinsic differences in the methane adsorption capacity. Those studies thus deeply reflect neither the essence of the adsorption nor the microcosmic adsorption behaviors of the methane on the organic-rich shales.

As a theoretical research approach for investigating the adsorption properties of adsorbents, molecular simulation methods, which are computer simulation methods for studying the physical chemistry characteristics of atoms and molecules that are able to investigate atomic-scale adsorption phenomena and properties between porous materials and fluid molecules, have attracted increasing attention in the past few years. Titiloye et al. [30], Yang et al. [31] and Xiong et al. [32] investigated the adsorption behaviors and transport properties of methane in montmorillonite pores using the grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) methods and discussed the influences of the pore size, temperature and water content. Jin et al. [33,34] and Kadoura et al. [35] studied the structural properties of carbon dioxide, methane, and their mixture in montmorillonite pores using the GCMC and MD methods and discussed some influence factors, including the pore size, temperature and water content. Sharma et al. [36] and Chen et al. [37] investigated the adsorption behaviors of methane and ethane in montmorillonite and illite pores, respectively, using the GCMC method. Xiong et al. [38] studied the adsorption behaviors of methane in quartz pores using the GCMC and MD methods. Liu et al. [39,40], Ambrose et al. [41] and Mosher et al. [42] adopted simplified modelsof these complex porous of organic-rich shales using an ideal graphite-based simulation cell to investigate the adsorption behaviors and structural properties of the methane in the pores using the GCMC and MD methods. Collell et al. [43], Zhang et al. [44] and Sui et al. [45] studied the adsorption behaviors and transport properties of methane on simplified kerogen isolated from organic-rich shales using the GCMC and MD methods, although the influence of the maturation level of the kerogen was not considered. In these studies, the GCMC and MD methods were proven to be effective in investigating the structural properties and adsorption behaviors of an adsorbate on an adsorbent, and they provided some knowledge on the methane adsorption on clay minerals (montmorillonite and illite), quartz and organic matter. However, there have not been enough reports to show that the comprehensive researches on the adsorption behaviors of methane on the organic matter and inorganic matter of organic-rich shales and the differences in the methane adsorption capacity on the organic matter and inorganic matter.

In our previous research [19], the total organic carbon (TOC) content of kerogen isolated from the Lower Silurian Longmaxi Formation shale was 78.5%, suggesting that there were higher carbon atom contents in the kerogen. The composition and structure of the kerogen is complex [46], and there was no effective way to construct a realistic model of the molecular structure of kerogen [47]. Many scholars [48–54] put forward models of the chemical structure of kerogen using different methods. These models only reflected the local structural characteristics of the molecular structure of kerogen but could not better analyze its physical and chemical characteristics, and thus they have not been widely used [47]. Some researchers [39–42] adopted an ideal graphite-based simulation cell to investigate the adsorption behaviors and structural properties of the methane, which is probably related to the higher carbon atom content of the kerogen. The maturation level of kerogen could impact the adsorption behavior of methane in the organic pores. As kerogen evolves during the maturation, the H/C and O/C atomic ratios are reduced. This process is reflected in the van Krevelen diagram [55], which can be used to distinguish between kerogen types based on the maturation. Therefore, in this work, to simplify the study, the kerogen would be simplified to ideal graphite, and oxygenated functionalized groups are grafted onto the graphite surfaces to obtain different O/C atomic ratios, which indicate varying maturation levels of the kerogen [56].

The mission of this article is to investigate the adsorption behaviors of methane on the organic matter and inorganic matter of organic-rich shales by experiments and molecular simulation. We investigated the pore structure and adsorption characteristics of the minerals and isolated kerogen, and the influences of the isolated kerogen and the minerals on the methane adsorption capacity were discussed. In addition, we used the GCMC and MD methods to investigate the structural properties and adsorption behaviors of methane in different types of pores of organic-rich shales, including organic pores and inorganic pores. The skeleton patterns of the organic pores and inorganic pores were first built using molecular simulation methods, and the adsorption behaviors of the methane in the organic pores and inorganic pores were then investigated. On this basis, the structural properties of the methane in the organic pores and inorganic pores were studied. The differences in the methane adsorption capacity between the organic