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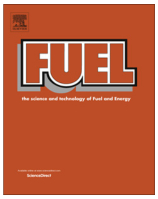

Full Length Article

Pore characterization and its impact on methane adsorption capacity for organic-rich marine shales

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ABSTRACT

Shale matrix pore structure controls the gas storage mechanism and gas transport behaviors. We employed various techniques to characterize the complex pore structures of 12 shale samples collected from two marine shale formations in upper Yangtze area (UYA) in China. The characterization techniques include field emission scanning electron microscopy (FE-SEM), high-pressure mercury intrusion porosimetry (MIP), and low-pressure N_2/CO_2 adsorption. The excess methane adsorption capacity was measured for each sample and the results were modeled using Langmuir model. Based on the FE-SEM image analyses, micro- and meso-pores within organic matter and inter-particle pores between or within clay minerals are the most commonly developed in these shale samples. Both uni- and multi-modal pore size distributions (PSDs) were observed, and a significant portion of pores are in the pore size range between 3 and 100 nm. It was also found that the micropore (<2 nm) is the major contributor to the overall specific surface area (SSA), whereas most of the pore volume is occupied by mesopores (2–50 nm). Two different fractal dimensions, pore surface fractal dimension (D_1) and spatial geometry fractal dimension (D_2), were estimated from low pressure N_2 isotherms, with D_1 ranging between 2.469 and 2.682, and D_2 ranging between 2.576 and 2.863, indicating that the surface and volume of pore structure are heterogeneous. Samples with higher D_1 can provide more adsorption sites for methane and tends to have relatively high adsorption capacity, whereas shales with higher D_2 do not influence the gas adsorption and storage capacities. Methane adsorption capacity increases with the increase of both micropore volume and micropore surface area, and this confirms that microporosity is the governing factor on methane adsorption capacity and storage.

1. Introduction

Shale gas has become one of the most important energy resources in recent years due to the advancement of well drilling and stimulation technologies. Unlike conventional gas reservoir rocks with micrometer-scale pores, shale is usually dominated by nano- to micrometer-scale pores and has extremely complex pore structure [1]. Pores in shale matrix can be classified into three groups, according to the pore classification system of the International Union of Pure and Applied Chemistry (IUPA): macropores (>50 nm), mesopores (2–50 nm) and micropores (<2 nm) [2]. Recently, the characterization of the complex pore structure of shale has drawn significant attention because the pore structure not only controls the gas storage capacity but influences gas transport dynamics [3–14]. Thus, the quantification of pore structure is critical and essential to estimate the gas storage capacity and to predict gas deliverability at reservoir conditions.

Various pore characterization techniques have been employed to quantify the total porosity, pore volume, specific surface area (SSA) and pore size distribution (PSD) of shale. Shale pore structure can be qualitatively characterized by advanced imaging techniques, including focused ion beam scanning electron microscopy (FIB-SEM) and field emission scanning electron microscopy/transmission electron microscopy (FE-SEM/TEM). These imaging techniques have been successfully used to define shale pore shapes, sizes and distributions [5,9,12,15]. The pore volume, SSA and PSD can be quantitatively measured by high-pressure mercury intrusion porosimetry (MIP), low-pressure N_2/CO_2 gas adsorption, and ultra-/small angle neutron scattering (USANS/SANS) [4,6,7,9,16–18].

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Fractal analysis has been used to quantify the irregularity and surface roughness of porous materials. It has been found that the heterogeneity of pore structures plays an important role in adsorption and diffusion processes [19–23]. Because the gas adsorption capacity is directly related to the irregularity of internal surfaces of shale pores, a surface fractal dimension can be used to depict the relationship between pore surface structure and gas storage capacity. Several pore characterization techniques can be potentially used to estimate fractal dimension, including FE-SEM, small angle X-ray scattering (SAXS), MIP and low-pressure N_2 adsorption [24–29]. It has been claimed that N_2 adsorption/desorption is a time- and cost-effective technique to quantify fractal dimensions [25,26,30,31]. Compared to the literature on the fractal characteristics of coal [23,26], few such studies exist for shale [32–34].

The upper Yangtze area (UYA) in China is well known as having a great production potential for shale gas. Two prospective marine shale units of Lower Cambrian and Lower Silurian age occur within UYA [35]. Both formations are considered as sweet spots for shale gas exploration because of their thickness, organic richness, widespread occurrence as well as favorable mineral composition [13,35,36]. However, little is known about methane sorption capacity and storage mechanisms in these two shale formations. Moreover, the detailed pore structure of these shales is not fully characterized. To provide a fundamental understanding of the pore structure and its impact on methane sorption capacity in UYA marine shales, we employed FE-SEM, MIP and low-pressure N_2/CO_2 adsorption to characterize the pore morphology, pore volume, SSA and PSD of the collected shale samples. In addition, fractal theory was used to quantify the heterogeneity of the pore structure based on low-pressure N_2 adsorption data. Combined with the high-pressure methane sorption results, the relationships between the gas sorption capacity and pore volume, SSA, and the fractal dimension were also analyzed and discussed. This study attempted to define the fundamental relationships between the pore structure and gas sorption capacity and laid the foundation for assessment of shale gas resources in UYA.

2. Experimental work

2.1. Sample collection and preparation

Fresh shale outcrop blocks were collected from the sweet gas production spots in UYA located in southwest China. In order to get the fresh samples, short-hole drillings with the depth of 10–60 m were used to obtain high quality outcrop shale samples. A map of sampling locations is shown in Fig. 1. A total of 12 marine shale samples including 7 samples from the Lower Silurian Longmaxi formation and 5 samples from the Lower Cambrian Niutitang formation were collected and prepared. The total organic carbon (TOC) content and methane adsorption capacity of each sample were previously measured in the lab and the results are listed in Table 1. The pore structure of each sample was then characterized by FE-SEM characterization, MIP, and low-pressure N_2 and CO_2 adsorption.

2.2. FE-SEM characterization

The FE-SEM imaging of nanopores was performed using the Quanta 200F equipped with an energy-dispersive spectrometer (EDS). In order to get better image quality, the surface of each shale specimen was prepared by Ar ion milling before the FE-SEM imaging. Following this, the pore structure of each specimen was characterized and analyzed based on the SEM images. The SEM imaging was carried out at a constant temperature of 24 °C and a humidity level of 35%. The qualitative nanopore structure information was interpreted from the obtained images [5] and the detailed results were presented in Section 3.1.

2.3. MIP pore characterization and measurements

The mercury intrusion measurements were conducted using a mercury porosimeter (Auto Pore IV 9510, Micrometrics Instrument) at pressures up to 60,000 psia. This in-house instrument is equipped in the Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, China University of Mining and Technology. Based on the standard operation guidelines, the pulverized shale samples were prepared and the diameters of shale particles were between 1 and 2 mm. Before MIP measurements, all shale samples were oven dried for over 3 h at constant temperature of 110 °C.

2.4. Low-pressure N_2/CO_2 adsorption characterization

Low-pressure (0–101.3 kPa) N_2 and CO_2 isotherm analyses were performed at the Key Laboratory of Coal Preparation & Purification, China University of Mining and Technology. Prior to the N_2 and CO_2 adsorption experiments, samples were automatically degassed at ~110 °C for about 14 h in a vacuum oven. N_2 adsorption data were collected at 77 K and CO_2 adsorption data were collected at 273 K using Quantachrome Autosorb-1 on 60 mesh samples. The relative pressure (p/p_0) for N_2 and CO_2 adsorption ranges from 0.009 to 0.995 and 0.0001 to 0.032, respectively. During the analysis, an automatic equilibrium-detection algorithm was employed to determine when equilibrium had been achieved between the adsorbed and the unadsorbed phases prior to isotherm data collection. The N_2 data collected on crushed samples were interpreted using the multi-point Brunauer–Emmett–Teller (BET) model for SSA and Barrett–Joyner–Halenda (BJH) model for mesopore volume. The Dubunin–Radushkevich (D–R) model was used for micropore surface area and the Dubinin–Astakhov (D–A) micropore volume were estimated from the CO_2 adsorption analysis [4,6,38,39]. A detailed description of these theories can be found in elsewhere [40].

2.5. High-pressure methane sorption analysis

High pressure (up to ~8.5 MPa) methane sorption isotherms were collected using a volumetric sorption apparatus (IS-300 isothermal adsorption/desorption analyzer) manufactured by Terratek, USA. All experiments were performed at 30 °C. For each sample, 100–150 g of pulverized powder sample with particle size less than 60 mesh was used for the high pressure methane sorption measurement.

3. Results

3.1. Pore morphology analyses based on FE-SEM images

Qualitative analyses of pore morphology are informative for defining the microscopic pore structures. FE-SEM images show abundant nano-scale pores and a few micron-scale pores. Based on FE-SEM image analyses, the shale matrix pores can be classified into three categories: inter-particle (interP) pores which are located between mineral particles, intra-particle (intraP) pores which are located within mineral particles, and organic-matter (OM) pores that are intra-particle pores located inside the kerogen [41]. All of these pore types, along with microfractures, are common in marine shales. OM pores are well-developed in the samples and display such features as pit, oval and honeycomb shapes (Fig. 2a, d, and f). It is notable that these OM pores are either