Research paper

Factors influencing the specific surface areas of argillaceous source rocks

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ARTICLE INFO

ABSTRACT

This paper integrates methods of nitrogen adsorption (N_2-BET) and ethylene glycol monoethyl ether (EGME) to present a comprehensive understanding of the specific surface areas (SSAs) of bulk rocks and clay fractions (<2 μm) in argillaceous source rocks, and employs the X-ray diffraction method to discuss the characteristics and influence factors of SSAs of argillaceous source rocks in order to service for unconventional petroleum exploration and exploitation. The methods of N_2-BET and EGME can be used to obtain external surface area (N_2-BET SSA) and total surface area (EGME SSA) within argillaceous source rock, respectively, and the difference between the total and the external surface area yields the internal surface area (internal SSA). The internal SSA accounts for over 80% in EGME SSA. Silty mudstone and argillaceous siltstone have larger internal and external surface areas than mud-bearing siltstone. Further, clay minerals (smectite in particular) make the greatest contribution to the internal, external and total surface areas (especially the internal and total surface areas) of source rock, whereas detrital minerals and carbonate minerals have a negative effect on each specific surface area. What is noteworthy is the fact that an abrupt increase in carbonate mineral content results in remarkable decreases in internal and EGME SSAs. These features therefore indicate that the differences in rock constituents (clay, detrital minerals and carbonate minerals) and mineral compositions affect the variations in SSAs characteristics of argillaceous source rocks. By plotting the SSAs vs. depth in bulk rocks and clay fractions, the variation extent of SSAs in clay fractions is better than that in bulk rocks. For either bulk rocks or clay factions, the value of internal SSA/N_2-BET SSA changes abruptly from 20 in the shallow-part (above 1500 m) to 5–10 in the deep-part (below 2000 m). The evolution of minerals during diagenesis creates variability in the mineral content with burial depth, which causes a subsectional evolution of SSAs in the vertical. As the surfaces within argillaceous source rock are closely correlated with the occurrence of organic matter or hydrocarbon, analyses of the difference between internal surface area and external surface area give the result that the SSAs of argillaceous source rocks are influenced by the factors of rock types, mineral compositions, diagenesis, etc., so attention to specific mineral assemblage and burial depth are of great significance to enhance the success rate of petroleum exploration and development in argillaceous source rocks, particularly in the research of unconventional petroleum systems.

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1. Introduction

Specific surface area (SSA) is one of the important attributes of sediments or sedimentary rocks. The surface within sediments or sedimentary rocks, which is measured as SSA, is the principal place for the materials of the inorganic phase to interact with other phases such as organic matter, CO_2 and nuclear waste (Mayer, 1994a; Kennedy et al., 2002; Iglesias and Quiñones, 2008; Eseme et al., 2012), and it also plays an important role in organic matter accumulation and hydrocarbon occurrence in argillaceous source rocks. Previous studies have shown that the content of total organic carbon (TOC) is positively correlated with SSA in soils, surface sediments and black shale (Weiler and Mills, 1965; Suess, 1973; Tanoue and Handa, 1979; Mayer, 1994b;

Mayer and Xing, 2001; Kennedy et al., 2002; Kennedy and Wagner, 2011), whereas the fine-grained minerals, which are the principal contributor to the SSAs in sediments and sedimentary rocks, are of extraordinary significance to the organic matter enrichment (Weiler and Mills, 1965; Jenkinson and Rayner, 1977; Bergamaschi et al., 1997; Keil et al., 1998; Mayer, 1999; Dexter et al., 2008). In source rocks, over 70% of organic matters are found to be combined with fine-grained minerals as soluble organic matter (Guan et al., 1998; Cai et al., 2010; Ding et al., 2011), which indicates that the clay fractions in the source rocks are more important to the enrichment of organic matter. In unconventional petroleum systems such as shale gas, in which adsorption and dissociation are the main ways for hydrocarbon occurrence, hydrocarbon is adsorbed on the surface of clay mineral, organic matter and pores with adsorption capacity ranging from 40% to as high as 85% (Curtis, 2002; Mavor, 2003; Montgomery et al., 2005). From the close relationship between organic matter (or hydrocarbon) and SSA (or clay

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fractions), it can be seen that the SSA plays an important role in the organic phase enrichment in sediments or sedimentary rocks.

Source rocks or shale include different types of minerals, and different minerals have different crystal attributes, which makes an impact on the SSAs. For instance, smectite with its 800 m^2g^{-1} of SSA has a large internal surface area, whereas illite with its 30 m^2g^{-1} of SSA only has an external surface area (Murray and Quirk, 1990; Goldberg et al., 2001; Zhu and Cai, 2012). So it is important to focus on the variation in the mineral assemblage in source rocks to characterize the SSAs. Meanwhile, the surface adsorption within the source rock can be divided into physisorption and chemisorption (Wypych and Satyanarayana, 2004; Nilsson et al., 2011). It is generally believed that the physisorption mainly occurs on the external surface and chemisorption predominately on the internal surface. Therefore, distinguishing the characteristics of different SSAs is of great significance for understanding the adsorption characteristics of organic matter and hydrocarbon. In SSA measurement of sediments or sedimentary rocks, different methods such as the solution adsorption method or gas adsorption method can be used separately based on the complexity of the SSA constituent (internal surface area and external surface area) (Cerato and Luteneggerl, 2002; Santamarina et al., 2002; Kaufhold et al., 2010). However, each type of method has its own limitations in the SSA measurement (Yukselen and Kaya, 2006; Arnepalli et al., 2008; Zhu and Cai, 2012). Only by using effective methods can the features of specific surface areas of source rocks be understood systematically.

This paper presents a discussion on the features, patterns of development and influence factors of specific surface areas within argillaceous source rocks. Samples of bulk rocks and their clay fractions (<2 μm) were taken from the Tertiary of well S in Dongying Sag (Bohai Bay Basin, eastern China), and employed methods of physisorption (the nitrogen adsorption method) and chemisorption (the ethylene glycol monoethyl ether method) for SSAs measurement and X-ray diffraction for the content of mineral compositions. The investigation is of great significance to study the characteristics of organic matter and hydrocarbon occurrence in unconventional petroleum systems.

2. Materials and experiments

2.1. Samples

A total of 29 core samples of argillaceous source rocks (TOC ranged from 0.03% to 4.01%, with 1.49% on average) have been selected for testing, which were taken by sealed coring at depths of 1000–4000 m in the formations of Guantao (Ng, Miocene), Dongying (Ed, Oligocene) and Shahejie ($Es_{1/2/3}$, Oligocene) in well S of Dongying Sag, Bohai Bay Basin of eastern China. As there is no unified criterion to distinguish different rock types, many criteria have been established based on different aspects, such as texture, composition and structure (Liu et al., 2001; Jiang, 2003; Hickey and Henk, 2007; Loucks and Ruppel, 2007). In our work, the Bohai Bay Basin in eastern China is a terrestrial basin that is near the source, and thus it contains much more terrigenous detrital minerals. For this study, which is focused on the SSA of minerals, all the samples therefore can be categorized into three rock types based on the content of detrital minerals (Lu and Sang, 2002), which were 25–50% as silty mudstone, 50–75% as argillaceous siltstone, and 75–95% as mud-bearing siltstone.

The well S is located on a structural high in the Lijin sub-sag of Dongying Sag. Dongying Sag is one of the secondary tectonic units of the Jiyang depression, which is a Meso–Cenozoic rift basin developed from the paleotopographical background of Paleozoic basement rocks (Zhu et al., 2004). Four geological evolution stages occurred in the Dongying Sag, including the early stage of rifting (the Kongdian Formation), the middle stage of rifting (the lower-middle Shahejie Formation), the late stage of rifting (the upper Shahejie Formation–Dongying Formation), and the post-rifting stage (Neogene) (Zhu et al., 2004). Since the Tertiary, the Sag has developed a Kongdian Formation with intermittent

lacustrine sediments and a Shahejie-4 Formation with salt and saline lacustrine depositions (Zhang et al., 2011). In terms of the samples, the lower Es_3 is a deep lake facies; during the sedimentation of the middle Es_3, the Dongying delta developed rapidly toward the depocenter of the basin; until the late Es_3, fluvial-delta depositions covered most of the Sag (Zhu et al., 2004). Afterward, Es_2 deposited as a river–delta facies, and Es_1 deposited as a lake deposition (Zhang et al., 2005).

The samples were crushed to less than 3 mm and split into several aliquots: The first was an original sample, the second was cleaned by flushing with chloroform solvent for 72 h to remove organic matter (TOC ranged 0.01–2.36% with 0.98% on average after chloroform treatment) and dried naturally, and the third was crushed and ground for the clay fraction (<2 μm) separation using the natural sedimentation method. The chloroform-treated bulk samples and clay fractions were prepared for SSA measurement, and the original samples (bulk rocks and clay fractions) were made for X-ray diffraction.

2.2. Experimental methods

2.2.1. SSA measurement

The nitrogen adsorption (N_2-BET) method (Brunauer et al., 1938; Santamarina et al., 2002) and ethylene glycol monoethyl ether (EGME) method (Carter et al., 1965, 1986; Cerato and Luteneggerl, 2002) were employed separately to test the source rock and clay fraction to obtain the SSA:

N_2-BET method: It is used to measure the external surface area (N_2-BET SSA) by using the ASAP 2010 M + C automatic SSA instrument of Micromeritics in the USA, under the condition of liquid nitrogen temperature (77 K). The procedure is to take 0.1–0.3 g of sample and put it in the oven with 80 °C for 6 h or longer, then take out the sample and put it in the sample tube for predegassing, set the temperature for the heating bag to 80 °C and degass for not less than 6 h. The sample was weighed again before it was moved to the measurement device, and the test software was run according to the standard measurement program (Webb and Orr, 1997); in addition, the N_2-BET SSA of the sample was calculated by the multipoint BET method (thirteen points of relative pressure (P/P_0) ranging from 0.05 to 0.35 were collected).

EGME method: For the EGME procedure, a vacuum pump (with a vacuum pressure of 609 mmHg) and an electronic analytical balance (with an accuracy of 0.0001 g) were employed. Approximately 1 g of sample was weighed and put in the oven at 80 °C for 6 h or longer. It was then taken out and put in the aluminum tare (with a diameter of 5 cm and a height of 8 mm) and 3 ml EGME solution (analytical grade) was quickly added to the sample with a pipette and swirled gently until the sample was soaked. Afterward, the aluminum tares with mixture were placed in a sealed desiccator with EGME solution, calcium chloride ($CaCl_2$) and phosphorus pentoxide (P_2O_5) (both of them were analytical grade). The desiccator was evacuated for approximately one hour so as to remove water vapor. More than 8 h later, the tares were weighed after the desiccator was evacuated again; the process of evacuation was repeated, and they were weighed until a constant weight was attained (the mass difference between the two measurements was less than 0.0010 g). Finally, the total surface area (EGME SSA) of the sample was calculated based on the absorbed quantity of EGME molecules (the conversion factor is 2.86×10^{-4} g/m^2).

2.2.2. X-ray diffraction (XRD)

X'Pert-MPD diffraction instrument (Philips Corp.) was employed for XRD measurement. The test condition included copper butt, pipe pressure 30 kV, conduit flow 40 mA and scanning speed 2° (2θ) /min. At the beginning of the test, the sample needed to be ground with the grains of 320-mesh. The natural thin section of bulk rock (or clay fraction)