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Experimental investigation of the pore structure of triassic terrestrial shale in the Yanchang Formation, Ordos Basin, China

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ABSTRACT

The Yanchang Formation was deposited in a terrestrial environment in the late Triassic period. It consists of organic-rich shales that possess hydrocarbon resources for both conventional and tight gas sand plays in the Ordos Basin. The identified source rocks have become horizontal drilling targets as an active shale gas play. Although limited, the current study suggests that the physics of its porous media is far more complicated than that of marine shales in either North America or China, which calls for detailed characterization. In this study, a series of laboratory experiments were conducted on 20 samples from Chang 7 and Chang 9 members of the Yanchang Formation to characterize the pore structure of the terrestrial shale, including the mercury injection capillary porosimetry (MICP) test, low-pressure N_2 adsorption test, X-ray diffraction mineralogy (XRD) test, and geochemical analysis. Moreover, petrographical analysis was performed to obtain field-emission scanning electron microscopy (FE-SEM) images in order to identify different types of pores, as well as their correlations with mineral constituents and organic matter.

The mineralogical analysis (XRD) reveals that the major constituting minerals of the samples are clay minerals, followed by quartz and feldspar. In addition, the percentages of carbonate minerals are found to be relatively low, which is distinctively different from the mineral makeup of common marine shales. Pyrite exists in all samples, varying from 1% to 12%, while the total organic carbon (TOC) is in the range of 3.5–7.14% and the vitrinite reflectance (Ro) from 0.88 to 1.39%. The low-pressure N_2 adsorption analysis shows that the total pore volume (TPV) ranges from 0.180–5.236 $\times$ 10^{-3} cm^3/g, and the specific surface area (SSA) changes from 0.209 to 13.601 m^2/g. The pore size distribution (PSD) attained from the low-pressure N_2 adsorption test reveals multimodal peaks between the 1.8 nm and 3–8 nm intervals, suggesting that most of the pores are mesopores.

From the FE-SEM observations, it is discovered that the organic matter or pyrite nodules occupy the macropore space (3–10 μm) formed at current burial depths. Organic pores are found to have a pore size ranging from 30 to 50 nm. Moreover, inter-crystalline pores exist within pyrite nodules with a pore size from 0 to 50 nm. These observations are in good agreement with the bimodal pore size distribution measured from the low-pressure N_2 adsorption analysis. Furthermore, the formation of macropores is likely controlled by the interplay between multiple factors, such as clay content, silicate minerals, carbonate minerals, and organic matter. In conclusion, the findings of this study provide a better understanding of pore structures in terrestrial shales, and help to evaluate the storage capacity and transport capability of terrestrial shales, in general.

1. Introduction

Recently, as advanced techniques have continued to develop and improve in North America, unconventional reservoirs, such as shale gas, tight gas and CBM (coalbed methane), have been significantly focused on and perceived as new forms of fossil energy. The global geological reserves of shale gas have been estimated to be 456.24 $\times$ 10^{12} m^3 (Perry and Lee, 2007). In 2000, shale gas only occupied 1.6% of gas production in the United States (U.S.) (Wang and Krupnick, 2013), while the percentage jumped to 44% in

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2014 (EIA, 2015). Such a dramatic increase has encouraged many countries other than the U.S. to explore these resources, such as Canada, Poland, Argentina, and China (Chen et al., 2011; Clarkson et al., 2012a). The geological reserves of shale gas in China were estimated to be 134 × 10^{12} m^3 (MLR, 2012). Moreover, its total production of shale gas increased from barely 200 million m^3 in 2013 to over 4.4 billion m^3 in 2015 (Zhang and Cao, 2016). In the meantime, terrestrial shale gas was proven to exist in China after the first terrestrial shale gas well was drilled in the Ordos Basin, north China by the Shaanxi Yanchang Petroleum Corporation (Liu et al., 2013; Jiang et al., 2014).

Based on the environment of deposition, organic-rich shales are usually grouped into three categories: marine, lacustrine, and terrestrial shales (Hutton, 1987). Most of the recovered shale gas in the U.S. is produced from marine shales. In China, however, shale gas has been discovered and produced in all of these types of organic-rich shales, such as the lower Silurian marine shales of the Longmaxi Formation in the Sichuan Basin, the middle Cretaceous lacustrine shales of the Qingshankou Formation in the Songliao Basin, and the upper Triassic terrestrial shales of the Yanchang Formation in the Ordos Basin (Zou et al., 2013).

The pore structure of shale involves information regarding size, shape, and count. These properties largely govern the mechanical, seepage, and storage behaviors of shale gas or oil reservoirs. From previous investigations, the pore system is rather complicated, and consists of pores with a vast variety of sizes and shapes (Clarkson et al., 2012b; Hu et al., 2012; Josh et al., 2012; Clarkson et al., 2013; Kuila and Prasad, 2013; Wang et al., 2014; Lin et al., 2015; Jiang et al., 2016). Several approaches have been utilized to investigate the characteristics of the pore structure in shales with qualitative and quantitative methods. The former includes scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), focused ion beam scanning electron microscopy (FIB/SEM), transmission electron microscopy (TEM), nano-computed tomography (Nano-CT), and magnetic resonance imaging (MRI) (Prado et al., 1998; Bernard et al., 2012; Chalmers et al., 2012a,b; Loucks et al., 2009, 2012; Wei et al., 2013; Yang et al., 2013a). On the other hand, pore size distribution (PSD), total pore volume (TPV), and specific surface (SSA) can be evaluated by quantitative analysis. These are made accessible through the use of low-pressure gas adsorption/desorption analyses, mercury injection capillary pressure (MICP), helium pycnometry, nuclear magnetic resonance (NMR), and small angle and small ultra-small angle neutron scattering (SANS/USANS) (Chalmers and Bustin, 2007; Ross and Bustin, 2007, 2008, 2009; Chalmers et al., 2012a,b; Clarkson et al., 2012b, 2013; Tian et al., 2013; Yang et al., 2013b, 2017, 2014).

The aim of this study is to adopt both qualitative and quantitative methods in order to provide a comprehensive characterization of the pore structure of the Triassic terrestrial shale in the Yanchang Formation of the Ordos Basin. Field emission scanning electron microscopy (FE-SEM) was used to perform qualitative analysis to investigate the pore geometry. N_2 adsorption/desorption and mercury injection capillary pressure (MICP) were applied for the purpose of quantitative analysis. In this paper, the combined BJH model with an adsorption curve and non-local density functional theory (NLDFT) model with an equilibrium branch was used to obtain PSD of terrestrial shale samples from the Yanchang Formation. The SSA was calculated by the multipoint Brunauere-Emmette-Teller (BET) equation, while the TPV was estimated by the Barrette-Joynere-Halenda (BJH) model (Gregg and Sing, 1982). In addition, geochemical and mineralogical tests, such as the total organic content (TOC) test, the Rock-Eval test, and X-ray diffraction (XRD) analysis were carried out to provide evidence for the previously mentioned pore structure analysis. A thorough understanding of the pore structure in the studied sample as an example can produce valuable information for engineers to properly evaluate the storage capacity and transport capability of terrestrial shales.

2. Material and methods

2.1. Shale sample

The shale samples were collected from Chang-7 and Chang-9 of the upper Triassic Yanchang Formation from seven wells in the southeast Ordos Basin of China. All of the 20 samples were obtained at a depth from 1140–1750 m (Table 1). The samples were observed as black shale, visible with graptolite fossils. A specimen was prepared from each of the 20 samples for low-pressure N_2 adsorption, MICP, TOC, and XRD tests. FE-SEM imaging tests were conducted on four samples, in which their surfaces were polished by Ar-ion milling. Another 10 samples were investigated by Rock-Eval tests. A high pressure methane isothermal adsorption test was performed on six additional samples to elucidate the relationship between pore structure and excess adsorption.

2.2. Experimental methodology

The shale samples were crushed to a grain size of less than 0.15 mm (or 100 mesh) for X-ray diffraction (XRD) analysis. XRD analysis was performed with an XRD Terra rock and mineral analyzer at 30 kV and 0.3 mA with Cu radiation. The total organic carbon content (TOC, wt %) was determined by a LECO CS230 carbon/sulfur analyzer. The specimens were treated with HCL acid with a concentration of 4%–4.13% and distilled water for 24 h prior to the TOC tests. Rock-Eval pyrolysis was conducted on 17 specimens using an OGE-VI Rock-Eval analyzer. Approximately 2 g of crushed specimen was used for determination of the Rock-Eval parameters. Random vitrinite reflectance measurements were performed using a Vickers M17 Research Model 1 Microscope under oil immersion and reflected white light, following the organic petrography procedure regulated by ASTM (2011).

The specimens for SEM observation were firstly polished with 400 grit emery cloth, and then precisely processed by argon beam milling. Back scattered electron (BSE) images were acquired on a Hitachi FE-SEM SU8000 instrument, with an accelerating voltage of 2 kV and working distances of 1.6 mm–2.3 mm.

The MICP experiments were carried out using a Micromeritics AutoPore IV 9500 V1.05 porosimeter. Based on the pore size classification given by the International Union of Pure and Applied Chemistry (IUPAC) (Rouquerol et al., 1994), there existed three pore groups which were classified as micropores, mesopores and macropores, corresponding to pore diameters of less than 2 nm, between 2 and 50 nm, and more than 50 nm, respectively. The porosimeter covers a measuring range of pore size from 3 nm to 120 μm, whereas its effective and reliable range of measurement is for pore diameters larger than 50 nm (Bustin et al., 2008; Li et al., 2015), rendering it a useful tool for disclosing the geometric information of mesopores.

The low-pressure N_2 adsorption/desorption experiments were conducted using a Quantachrome Quadrasorb SI surface area analyzer and a pore-size analyzer. Crushed powders were sieved to approximately 2–5 mm and were dried at 378 K for 24 h in a vacuum oven. All of the N_2 adsorption-desorption isotherms were obtained under a relative pressure from 0.01 to 0.995 at 77 K. The specific surface area (SSA) was calculated by the multipoint Brunauer-Emmett-Teller (BET) method with a relative pressure range of 0.05–0.30 (Brunauer et al., 1938). The TPV was obtained by the Barrett-Joyner-Halenda (BJH) equation (Gregg and Sing, 1982). In addition, the average pore size was calculated by TPV and SSA.

The isothermal adsorption measurements were performed with