Evolution of nanoporosity in organic-rich shales during thermal maturation

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H I G H L I G H T S

- Laboratory-matured shale samples were produced by an anhydrous pyrolysis experiment.
- Low-pressure gas adsorption was used to characterize the pore structure of laboratory-matured shales.
- There are substantial differences in evolution of nanoporosity between organic-rich and organic-poor samples.
- Evolution of organic matter-hosted nanopores of gas shales can be roughly divided into three stages.

A R T I C L E   I N F O

A B S T R A C T

Artificial shale samples with equivalent vitrinite reflectance values (VRo) ranging from 0.69% to 4.19% were obtained from an anhydrous pyrolysis experiment. Microporous and mesoporous characteristics of these samples were investigated by low-pressure nitrogen and carbon dioxide adsorption techniques. The result shows that the nanoporosity (microporosity plus mesoporosity) increases with thermal maturity after the oil window stage, and this increase is attributed to the formation of porosity within organic matter and/or mineral–organic matter groundmass, rather than in the pure clay minerals. By combining the gas generation and porosity evolution of these shales, a general model for formation and development of the nanoporosity is proposed.

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1. Introduction

A gas shale reservoir is characterized by abundant pores having sizes in a range of several to several hundreds of nanometers [1–8]. Pores are subdivided into micropores (pore width <2 nm), mesopores (pore width between 2–50 nm) and macropores (pore width >50 nm) according to the classification of International Union of Pure and Applied Chemistry (IUPAC) [9]. It has been found that a considerable part of gas occurs in an adsorbed state within micro- and mesopores of gas shales [3,4,10–12]. Elucidating the complex pore networks in gas shales has become a strategic subject because many studies have shown that shale pore structure is one of the most important factors controlling gas capacity [1–4,10–12]. Several measurement techniques have successfully been developed to characterize the complex pore systems such as small-angle and ultra small angle neutron scattering (SANS/USANS), low-pressure gas adsorption, mercury injection capillary pressure (MICP), and scanning electron microscopy (SEM) [5,13–17]. The geological controls of pore structure in gas shales include the total organic carbon (TOC) content, thermal maturity and mineralogy, which have preliminarily been discussed in previous works [3,4,10,18,19].

Effect of thermal maturation on porosity has recently attracted more attention because of the growing recognition that porosity in organic matter, to a large extent, is a function of thermal maturity [4,6,18,19]. The recent efforts toward understanding porosity evolution with maturation have been matched with documenting the pore networks in gas shales. For example, Curtis et al. [20] used focused ion beam milling combined with scanning electron microscopy (FIB–SEM) techniques to investigate the organic porosity within Woodford Shale samples with vitrinite reflectance values (VRo) ranging from 0.51% to 6.36%, finding that secondary organic porosity is absent in samples with VRo values less than 0.90%, but does occur in samples with VRo values greater than 1.23% except for a 2.0% VRo sample. The exception suggested that maturity alone is not a reliable predictor of porosity in organic matter and other factors such as organic matter composition

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complicate this predication. While SEM observations of organic-rich mudstones from the Upper Jurassic Kimmeridge Clay Formation indicate that there are no differences of organic pore shape and size between immature and mature samples, and the minimal preservation of organic pores during hydrocarbon generation is attributed to the highly ductile nature of clays and organic materials [21]. Mastalerz et al. [22] examined the evolution of porosity with maturation in a suit of five New Albany Shale samples spanning a maturity range from immature (VRo = 0.35%) to postmature (VRo = 1.41%), observing that total porosity and total pore volume exhibit a significant decline from immature sample to late mature sample with a reduction of more than 80%, and then regain their higher values in the post mature sample. After addressing the influence of TOC content and mineralogy on porosity, they further suggested that maturity appears to exert the dominant control upon porosity development in shales. However, their data was limited to shales with VRo value less than 1.41%.

Therefore, response of shale porosity, especially organic porosity to hydrocarbon generation and cracking caused by thermal maturation remains puzzling in gas shale systems (especially highly-matured shales), additional systematic studies need to be carried out. In the present study, three suites of artificial shale samples across a maturation gradient were produced by laboratory anhydrous pyrolysis of three low maturity shale samples with different kerogen types or TOC contents at a wide range of temperatures. The evolution of their micro- and mesoporous characteristics with thermal maturation was evaluated by low pressure nitrogen and carbon dioxide adsorption measurements. The relationship between gas generation and nanopore formation is also discussed.

2. Samples and experiments

2.1. Samples

Three suites of shale samples covering a range of maturities were produced by anhydrous pyrolysis of three low maturity shales/mudstones (approximately 0.60% VRo). The starting samples used to be pyrolyzed originated from three different deposits across China, including two organic-rich shales (samples LCG and DL) and one organic-lean mudstone (sample EP). Sample LCG was collected from an Upper Permian outcrop (Yaomoshan, Urumqi) of the southern Junggar Basin, sample DL from an Upper Permian outcrop (Changjianggou, Guangyuan) in the northern Sichuan Basin, and Sample EP from an Oligocene deposit of well WC19-1M-1 in the western Pearl River Mouth Basin. Their locations were present in the Refs. [23–25]. A coal sample with a similar initial maturity (VRo = 0.56%) was also pyrolyzed under the same conditions as the three shales to give a measure of the thermal maturity of the shale samples at different pyrolysis temperatures.

2.2. Anhydrous pyrolysis

The anhydrous pyrolysis experiment was carried out under inert conditions in a programmed muffle furnace. The four raw samples were first crushed to <250 μm, dried for 24 h at 60 °C in a vacuum oven, and then each was separated into 10 fractions, transferred to a series of quartz tubes (with an inner diameter of 30 mm) and sealed under vacuum condition. The four raw samples were simultaneously heated in the furnace from room temperature to a preset temperature at a heating rate of 200 °C/h, and then kept for 24 h. The target temperature was set within a range of 300–750 °C at 50 °C intervals. Every heating run was performed on a new batch of powdered samples. The pyrolysis products at each temperature point were recovered and were subject to an ongoing multidisciplinary analytical program.

2.3. Organic geochemistry and petrology analysis

The total organic carbon (TOC) of the three initial shales was measured by a Leco CS230 Carbon/Sulfur analyzer after the samples were treated by hydrochloric acid to remove the carbonates. The Rock–Eval pyrolysis was conducted using a Rock–Eval 6 Turbo analyzer to assess their hydrocarbon generation potential. Standard IFP55000 was applied to calibrate the instrument before and after sample analyses.

A 3Y-Leica DMR XP microscopy equipped with a microphotometer was used to identify the macerals of the initial shales and measure the vitrinite reflectance (VRo) values of the coal samples obtained from the different pyrolysis temperatures. According to the maturities achieved from different pyrolysis temperatures, a standard with a reflectance closest to the measured value was selected from three available standards: yttrium aluminum garnet YAG-08-57 (Ro = 0.904%), NR1149 (Ro = 1.24%), and cubic zirconia (Ro = 3.11%). An oil objective of 50 × /0.85 and a measuring fiber with a diameter of 0.6 mm were employed. VRo% for each sample was determined by averaging 50 measurements on vitrinite particles.

2.4. Mineral composition analysis

X-ray diffraction (XRD) analysis of the shale powders (including the three initial shales and some of their heated samples) was carried out on a Bruker D8 Advance X-ray diffractometers at 40 kV and 30 mA with a Cu Kα radiation (λ = 1.5406 for Cu Kα1). Stepwise scanning measurements were performed at a rate of 4°/min in the range of 3–85° 2θ. The relative mineral percentages were estimated semi-quantitatively using the area under the curve for the major peaks of each mineral with correction for Lorentz Polarization [4].

2.5. Gas adsorption and data analysis

Nitrogen adsorption at 77 K is universally used to examine the micro-, meso-, and macroporosity of solid materials if a wide range of relative pressures (P/P_0) were applied [26]. Carbon dioxide adsorption at 273.15 K is often the preferred choice to investigate the microporosity of carbonaceous materials, since the ambient temperature promote the gas diffusion in the microporous system compared to the low temperature (77 K) used in nitrogen adsorption [26]. However, a limitation of CO_2 adsorption at 273.15 K is that CO_2 molecular cannot fill larger micropores and also may have additional interactions with organic matter [26,27]. With more attention focused on the shale pore systems, nitrogen and carbon dioxide adsorption techniques have widely been introduced to study the pore characteristics of shales [5,13–17]. The experimental methods and parameter calculations may be briefly described as follows.

Low-pressure gas adsorption measurements were conducted on a Micromeritics ASAP 2020M surface area and porosimetry analyzer. Nitrogen adsorption and carbon dioxide adsorption were used to obtain information about meso- and micropores respectively. The term "nanopore" or "nanoporosity" used in this article referred in particular to the micropores and mesopores. Each sample was degassed at 110 °C for 16 h in a vacuum chamber prior to the analysis to remove its residual volatile material. Nitrogen isotherms were collected within a relative pressure (P/P_0) range of 0.01–0.995 at liquid nitrogen (77 K). The equivalent surface area was calculated within a relative pressure range of 0.05–0.20 by the multi-point BET (Brunauer–Emmett–Teller) equation [28]:

$$\frac{1}{V(P_0/P - 1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{P}{P_0} \tag{1}$$