Formation and evolution of nanopores in organic-rich shales: Insights from the hydrous pyrolysis experiments in a closed system

Chuxiong Li¹²,³, Qilin Xiao¹², Qi Chen¹, Xinchao Jiang¹²

¹ College of Resources and Environment, Yangtze University, Wuhan 430100, China
² Key Laboratory of Oil and Gas Resources and Exploration Technology, Yangtze University, Wuhan 430100, China
³ Wuxi Research Institute of Petroleum Geology, Sinopec Exploration and Production Research Institute, Wuxi 214126, China

E-mail addresses: 2279724044@qq.com (C. Li), qilinxiao@cug.edu.cn (Q. Xiao)

Abstract. In order to make a better understanding of the formation and evolution process of nanopores in organic-rich shales with increasing thermal maturity, an early mature oil shale from the Nenjiang Formation in Changle Depression of Songliao Basin was pyrolyzed with the presence of brine water in a closed system. The measurements of TOC, XRD, N₂ adsorption were conducted on the initial and pyrolyzed samples. The results show that the development of nanoporosity within pyrolyzed shales can be divided into three phases with thermal maturity increasing: the intensive increase (Rₙ=0.61–2.09%), slight decrease (Rₙ=2.09–2.47%) and slight increase (Rₙ=2.47–4.01%). The significant occurrence of nanopores was associated closely with intensive hydrocarbon generation and expulsion at the mature to high mature stages, liquid hydrocarbons filling into the nanopores restrict their developments. The formation of pyrobitumen by oil secondary cracking at the early over mature stage decrease the occurrence of micropores and macropores, and hence reducing the pore volumes. The secondary phase of nanopores formation is at the late over mature stage, which is attributed to the mineral transformation and limited capability of hydrocarbon generation and expulsion. This study should be helpful in evaluating shale oil and gas resources in nature.

1. Introduction

The organic-rich shales in sedimentary basins are considered to be both source rocks and hydrocarbon reservoirs [1]. Pore networks in shale reservoirs provide effective space for hydrocarbon storage and adsorption [1]. In comparison with conventional reservoirs, shale reservoirs are dominated mainly by ≤100 nm nanopores [2]. The formation and evolution process of nanopores within organic-rich shales has been one of the key issues in the field of unconventional shale oil and gas resources, which is the integrated results of various geological and geochemical elements in the subsurface within sedimentary basins [3].

In general, two methods are believed to be reasonable to obtain shale samples with increasing thermal maturity levels. The first way is to collect natural samples within sedimentary basins; the second method is to artificially pyrolyze the immature shale samples in the lab. The latter is considered to be much better relative to the first one, since it can provide a relatively accurate and
controllable ambient environment to eliminate the impacts of the heterogeneity of natural shale samples. In order to make a better understanding of the formation and evolution process of nanopores in organic-rich shales with increasing thermal maturity, a series of pyrolysis experiments were conducted on an early mature shale sample from the Nenjiang Formation in Changling Depression of Songliao Basin by using the hydrous pyrolysis experiments in a close system, shale samples with the thermal maturity levels from early mature to over-mature were obtained, the measurements of TOC, XRD, N₂ adsorption have been done on these samples to disclose the occurrence and evolution process of nanopores within organic-rich shale reservoirs.

2. Samples and methods

2.1. The initial shale sample
The initial shale sample was selected from the Nenjiang Formation in Changling Depression of Songliao Basin in south China. It contains 8.16% TOC and type I kerogen with the thermal maturity levels of R₀=0.61%. The mineral composition is mainly consist of quartz, followed by feldspar and clay minerals as well as a little bit of pyrite.

2.2. Pyrolysis experiments
The experiments were conducted in stainless-steel Hastalloy C-22 reactors. In each experiment, 10–20 g of rock chips were loaded into the reactor with the same quantity of salty water and purged with argon for 15 min and then sealed and put into the oven. The oven temperatures were 350–600 °C monitored with type E thermocouples. All experiments were conducted for 12–84 h (Table 1). The reactors were open after cooling down to room temperature. The rock samples were collected for the subsequent measurements. The thermal maturity levels of these shales were determined by using the hydrous pyrolysis experiments on an early mature coal sample (R₀=0.60%) at the same experimental conditions. These samples were divided into two parts, and the first part was extracted by using organic solvents.

Table 1. The conditions of pyrolysis experiments and the relevant thermal maturity levels

| Sample | Temperature (°C) | Heating time (h) | R₀ (%) | Maturity stage |
|--------|-----------------|-----------------|--------|----------------|
| Y-1    | 350             | 16.8            | 0.61   | early mature   |
| Y-2    | 400             | 12.0            | 1.06   | mature         |
| Y-3    | 400             | 25.2            | 1.36   | mature         |
| Y-4    | 400             | 84.0            | 1.76   | high mature    |
| Y-5    | 450             | 12.0            | 1.88   | high mature    |
| Y-6    | 450             | 24.0            | 2.09   | over mature    |
| Y-7    | 450             | 72.0            | 2.29   | over mature    |
| Y-8    | 500             | 72.0            | 2.47   | over mature    |
| Y-9    | 550             | 72.0            | 3.00   | over mature    |
| Y-10   | 600             | 24.0            | 3.67   | over mature    |
| Y-11   | 600             | 24.0            | 4.01   | over mature    |

2.3. LECO TOC
TOC was measured by LECO CS-200 analyzer on the samples with <200 mesh after treated with hydrochloric acid to remove the carbonates.

2.4. Vitrinite reflectance (R₀)
The vitrinite reflectance was measured by 3Y microphotometer. According to different thermal maturity of the sample, yttrium aluminium garnet (Ro=0.904%) and cubic zirconia (Ro=3.11%) were used as standard samples. Under the condition of oil immersion, the refractive index N=1.515 and objective lens X50/0.85 were used to measure 50 different vitrinite particles of the same sample to obtain the vitrinite reflectance average value.

2.5. X-ray diffraction (XRD)
Shale powders with <200 mesh were used to do X-ray diffraction (XRD) analysis on a Bruker D8 Advance x-ray diffractometers at 40 kV and 30 mA with a Cu Kα radiation (λ = 1.5406 for CuKα1). Stepwise scanning analysis was performed at 4º/min within 3º–85º (2θ). The relative mineral composition was evaluated by using the major peak areas of the specific minerals.

2.6. Gas adsorption
Gas adsorption measurements were performed on an Autosorb-iQ-MP instrument (Quantachrome Instruments) equipped with a vacuum pump capable of reaching 5E-7 Pa (7.25E-11 psi). Samples were crushed to 60–80 mesh size and then placed into 6-mm stem quartz sample cells and degassed for 12 h at 110°C under vacuum. Nitrogen at -196.15°C was used as the probe gas for all experiments. Specific surface areas were calculated using the best linear range between 0.05 and 0.3 pressure/initial pressure (P/Po) of N₂ adsorption, with a minimum of five points used in the Brunauer–Emmett–Teller [4] (BET) surface-area analysis. Pore volumes and pore size distributions were obtained using the Barrette Joyner Halenda [5] method (BJH) and the BET [4] method.

3. Results and discussion

3.1. TOC and mineral compositions
The LECO TOC is 8.16% for the unheated initial shale sample and decreases to 3.12% at the end of pyrolysis experiments, implying the high conversion of around 62% for type I kerogen within this shale (Figure 1). For the unextracted samples, The TOC value decreases gradually with thermal maturity increasing. The significant difference in TOC can be observed on the samples before and after the organic solvents extraction at the oil to early wet gas windows (Ro=0.61–1.88%), indicating the impacts of significant liquid hydrocarbon generation and then filling in nanopores. The obvious increase of TOC for the extracted samples at the early wet gas window (Ro=1.36–1.88%) indicates the intensive oil cracking to form pyrobitumen, which is generally consistent with previous study [6].

The initial sample contains 66.0% quartz, 13.0% feldspar, 5.8% illite, 2.2% chlorite, 12.0% I/S mixed layer and 1% pyrite, and a little bit of carbonate. For the pyrolyzed samples, illite has a significant increase, an obvious decrease is present on the I/S mixed layer, indicating the transformation of the I/S mixed layer to illite, slight decreases of quartz and pyrite indicate the occurrence of quartz and pyrite dissolution under the experimental conditions (Figure 1).

Figure 1. Plots showing LECO TOC (a) and mineral compositions (b) change with thermal maturity increasing
3.2. N\textsubscript{2} adsorption and desorption isotherms

Figure 2 shows the N\textsubscript{2} adsorption and desorption isotherms of the unextracted and extracted samples. According to the IUPAC classifications\cite{7}, all the isotherm curves are type IV with a H3 hysteresis loop. This indicates the occurrence of slit-shaped or wedge-shaped nanopores within the shales. In general, N\textsubscript{2} adsorption volume increases with the thermal maturity increasing and its significant increase presents at the early to mature stages (R\textsubscript{o}=0.61–1.36\%). The obvious difference in N\textsubscript{2} adsorption volume between the unextracted and extracted samples is shown on the samples with thermal maturity levels of R\textsubscript{o}=1.06–1.88\% and the extracted samples generally have higher N\textsubscript{2} adsorption volumes. This indicates shale samples contain more solvable liquid hydrocarbons at these maturity stages, which is consistent with the results of TOC analysis as shown in Figure 1. Little change can be detected on the over mature samples in dry gas generation window. This is attributed to little liquids left within these samples.

![Figure 2. Isotherms of N\textsubscript{2} adsorption and desorption of initial and pyrolyzed shale samples before and after solvent extraction](image)

3.3. Pore size distribution

The pyrolyzed samples are enriched in various nanopores, in particular the pores with the diameters of <10 nm (Figure 3). The significant occurrence of nanopores takes place at the mature to over mature stages (R\textsubscript{o}≥1.0\%) as indicated by the rapid increase of the abundance of micropores, mesopores and macropores. The hydrocarbon charging into nanopores within shale samples impacts the development...
of micropores and mesopores with the diameters of 2–20 nm as suggested by the significant enrichment of these pores after organic solvent extraction within the pyrolyzed samples with thermal maturity of \( R_o = 1.06–1.88 \% \), and presents little impacts beyond this range.

![Figure 3. The plot of \( \frac{dV}{dD} \) (a, b) and \( \frac{dV}{d\log(D)} \) (c, d) versus D using BJH model. (a and c, before solvent extraction; b and d, after solvent extraction)](image)

3.4. Pore volume and Specific surface area

The variations of pore volumes and specific surface areas reflect the formation and evolution of nanopores in shale samples at a much larger scale [8]. For the unextracted samples, the total pore volume generally changes with three phases as thermal maturity increasing: the intensive increase \(( R_o = 0.61–2.09 \%)\), slight decrease \(( R_o = 2.09–2.47 \%)\) and slight increase \(( R_o = 2.47–4.01 \%)\). Specifically, the macropore volume has the similar change trend as that of the total pore volume. This suggests the dominated effects of macropores on the total pore volume; the mesopore volume shows the continuous increase at \( R_o = 0.60–2.47 \% \) and slight decrease at \( R_o = 2.47–4.01 \% \), indicating the transformation of mesopores into macropores within the samples at \( R_o = 2.47–4.01 \% \), which is consistent with previous study [8]; the micropore volume also varies with three phases: the slight increase \(( R_o = 0.61–1.76 \%)\), slight decrease \(( R_o = 1.76–2.47 \%)\) and slight increase \(( R_o = 2.47–4.01 \%)\). In comparison with the unextracted samples, the decrease of the total pore and macropore volumes for the extracted samples occur much earlier with \( R_o = 1.36–2.09 \% \), and that of mesopore volume also take place earlier with \( R_o = 1.76–4.01 \% \) (Figure 4a).

The nanopore surface area shows an intensive increase at \( R_o = 0.61–1.76 \% \) and slight increase at \( R_o = 1.76–4.01 \% \) for the untreated samples and presents a significant increase at \( R_o = 0.61–1.76 \% \) and then obvious decrease at \( R_o = 1.76–4.01 \% \) for the treated samples. The mesopore surface area shows the similar changing pattern, indicating the controlling effects of mesopores on pore surface area. The other pore surface areas generally have the similar trends as their volumes (Figure 4b).

These results indicates that hydrocarbon generation and expulsion and oil cracking to form solid pyrobitumen have critical impacts on the occurrence of nanopores within organic-rich shales with thermal maturity increasing, since the initial increase in the total pore, macropore and micropore volumes corresponds to the significant generation and expulsion of liquid hydrocarbons, their decrease corresponds to the main stage of pyrobitumen formation. The illitization of I/S mixed layers and quartz dissolution still have an important impact on the development of nanoporosity as indicated by their intensive changes at the over mature stage.
Figure 4. Plots showing pore volume (a) and specific surface area (b) change with increasing thermal maturity. (SE = Solvent extraction)

4. Conclusions

The development of nanoporosity within organic-rich shales can be divided into three phases with thermal maturity increasing: the intensive increase (Ro=0.61–2.09%), slight decrease (Ro=2.09–2.47%) and slight increase (Ro=2.47–4.01%). The significant occurrence of nanopores is caused by intensive hydrocarbon generation and expulsion. The formation of pyrobitumen by oil secondary cracking at the early over mature stage restricts the occurrence of micropores and macropores, and hence reducing the pore volumes. The secondary phase of nanopore formation is due to the mineral transformation and hydrocarbon generation and expulsion at the late over mature stage.

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