Exploring the coupling relationship between hydrocarbon generation of continental shale and nanopore structure evolution—A case study of Shahejie formation in Bohai Bay Basin

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Received: 23 May 2021 / Accepted: 23 September 2021 / Published online: 9 October 2021
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Abstract

The nano-scale pore structure of shale is closely related to the self-generated and self-accumulated shale oil and gas. The Bohai Bay Basin is a crucial oil-bearing basin in eastern China, and the Paleogene Shahejie Formation is the most important source rock section in this area. In order to study the internal relationship between hydrocarbon generation evolution and pore structure characteristics of source rocks, we conducted hydrocarbon generation simulation tests with a closed gold tube system, and heated up original rocks from Shahejie Formation in Laizhou Bay Sag, southern Bohai Bay Basin, from 290 °C to 440 °C at different heating rates. Besides, we carried out low-temperature N₂ adsorption experiments on sample residues, and measured their pore structure characteristic parameters. The results show that with the increase of simulated temperature, the specific surface area and pore volume of nano-pores below 10 nm (which are mainly organic pores) decrease first and then increase, while those of nano-pores above 10 nm increase all the way. The evolution trend of total specific surface area and pore volume is mainly controlled by pores below 10 nm which are mainly organic pores, especially micropores below 2 nm. There are two main factors affecting the development of inorganic pores: (1) Dissolution of organic acids produced by pyrolysis of organic matter in hydrocarbon-generation evolution; (2) Deformation of crystal structure of mineral components under the combined action of temperature and pressure. The experimental results at different heating rates demonstrate that rapid settlement under geological conditions is not conducive to the development of nano-pores, especially micro-pores composed of organic pores.

Keywords Continental shale · Hydrocarbon generation · Nanopore structure · Shahejie formation · Bohai Bay Basin

Introduction

Unconventional oil and gas, represented by shale oil and gas, affect the global energy structure profoundly. However, due to factors such as tight shale reservoir and poor permeability, prediction of sweet spots of shale oil and gas resources has become a major problem. Its reservoir space is dominated by nano-scale pores in shale, and the reservoir modes mainly

include adsorption state, free state and dissolved state (Curtis 2002; Montgomery et al. 2005; Jarvie et al. 2007; Ross and Bustin 2009; Li et al. 2014; Zhao et al. 2020). The pore structure of shale is the key factor to determine whether the fluid exists in adsorbed or free state. The mobility study of shale oil in Zhanhua Sag pointed out that movable shale oil mainly exists in pores with pore size above 50 nm (Jiang et al. 2020). For pores below 50 nm, they have a large specific surface area and poor connectivity, making shale oil absorbed on the pore surface and thus difficult to flow. In fact, with the change of fluid composition caused by the increase of thermal evolution, the critical pore size will also change. A large number of studies show that the mobility of shale oil is positively correlated with the total pore volume, total effective pore volume and average pore diameter of reservoir. (Huang et al. 2018; Li et al. 2019; Ning et al. 2020).

Shale pores are divided into organic pores, mineral matrix pores and micro-fractures, and the first two types are

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directly affected by the evolution of hydrocarbon generation (Loucks et al. 2009). During this process, with the hydrocarbon generation and expulsion, the structure of organic matter changes and then forms organic pores. These pores are affected by the type and maturity of organic matter (Sun et al. 2015; Topór et al. 2017). On the one hand, the development of mineral matrix pores is influenced by diagenetic evolution. On the other hand, it is also reformed by hydrocarbon generation from organic matter (Jiang et al. 2017; Wang et al. 2017; Wu et al. 2017). Through the hydrous simulation experiment, it is found that the pore evolution of shale changes little with the increase of thermal maturity, and the rapid formation of secondary pores is at the peak of oil generation (Sun et al. 2015). At this stage, the specific surface area and pore volume of nano-pores increase with the degree of thermal evolution. Wu et al. (2015) pointed out that the nanopore of continental shale decreased rapidly in the early stage of hydrocarbon generation due to compaction. Then, it increased dramatically after entering the stage of rapid hydrocarbon generation due to the generation of a large amount of oil and gas and the compaction of clay minerals.

The third member of Shahejie Formation in Bohai Bay Basin has great resource potential of shale oil and gas. But there is little research on the relationship between pore structure characteristics and hydrocarbon generation evolution in this area. This paper makes a detailed study on the hydrocarbon generation evolution characteristics and pore structure development process of the source rocks through the simulation experiment of gold tube hydrocarbon generation in a closed system and low temperature N₂ physical adsorption experiment. It aims to explain the internal relationship between nano-pore structure and hydrocarbon generation evolution, and provide technical reference for exploration and development of shale oil and gas resources in this area.

Samples and experiments

Samples

The samples in this study are collected from the carbonaceous mudstone of the third member of Shahejie Formation in Laizhou Bay Sag, Bohai Bay Basin. The basic geochemical characteristics of the samples are shown in Table 1.

Experiments

The samples are ground to granules under 100 mesh by a crusher. After the dissolved organic matter is removed by Soxhlet extraction, the samples are put into a gold tube (40 mm × 2.5 mm × 0.25 mm) and sealed by argon arc

Table 1 Basic geochemical characteristics of samples

Sample	TOC	S1	S2	S3	Tmax	HI	quarz	Anorthoe	Calcite	Dolomite	Grey matter	Pyrite	Clay	I/S	It	Kao	C	Mixing ratio
K-93	5.52	0.36	20.02	0.73	437	465.58	19.5	–	24.4	–	24.4	4.3	51.8	57	35	6	2	40

welding in argon atmosphere. The weight of the samples in each gold tube ranges from 450 mg–800 mg. The sealed sample is put into a stainless steel autoclave and heated in a high-temperature pyrolysis furnace. We use a pressure parallel device to keep the experiment pressure at 50 MPa, with an error of ± 2 MPa. Here is the temperature rise process: First, the temperature is increased from room temperature to 250 °C in 10 h. Then we raise it to the target temperature at two heating rates, 2 °C/h and 20 °C/h, respectively. The temperature error is ± 1 °C. Samples are taken according to the set temperature points, and each heating rate has 7 temperature points. More details about simulation experiments can be found in previous studies (Fu et al. 2020; Tian et al. 2008; Wang et al. 2013).

Quantification of hydrocarbon generation rate

After the simulation experiment, we analyze the gas composition on HP7890A gas chromatograph equipped with Walson ECE module. Specifically, we put gold tubes into the vacuum pumping system and puncture them with a steel needle, as external standard method after gas chromatography. Chromatographic column model is HP-AL/S (25 m $\times$ 0.32 mm $\times$ 8.0 μ m), and helium is used as the carrier gas. The heating procedure is as follows: The initial temperature is kept at 60 °C for 3 min. Then, it is raised to 190 °C at a rate of 25 °C/min, the temperature remains unchanged for 3 min.

C_{7+} component analysis is divided into C_{7-14} and C_{14+} . For C_{7-14} , after the gas component analysis, the remaining gas in the system is frozen in a 4 mL sample bottle with a liquid nitrogen cold trap, and n-hexane solvent is added. Then we cut the gold tube and soak it in the solvent to fully

dissolve C_{7-14} , which is quantitatively analyzed in Agilent 7890A gas chromatograph with deuterated C_{24} alkane as internal standard. The chromatographic column model is DM-5(30 m $\times$ 0.32 mm $\times$ 0.25 μ m), and helium is used as the carrier gas. The heating procedure is as follows: The initial temperature stays at 40 °C for 5 min. Then, it is raised to 290 °C at a rate of 4 °C/min and the temperature remains unchanged for 15 min. When the analysis is completed, let the sample stand. After n-hexane volatilizes completely, add dichloromethane and make the sample stand for 72 h. Then, we conduct 30 min' ultrasonic treatment. After that, the residue of the samples are filtered to obtain the constant weight of C_{14+} components and then the filtered samples are weighed. Finally, the above two components are added to obtain total C_{7+} .

Pore structure analysis

The pore structure of the solid residue obtained by filtration is analyzed by N_2 adsorption experiment at low temperature. During the experiment, we adopt the ASAP2460 automatic physical adsorption instrument produced by Micromeritics. Without further treatment, the solid residue is directly put into a sample test tube and degassed in vacuum at 110 °C for more than 24 h. Then, nitrogen is introduced in stages at -191.2 °C for adsorption–desorption experiment. According to the nitrogen adsorption capacity of the samples under different pressure conditions, we calculate the specific surface area of the samples by multi-point BET model linear regression, and obtain the pore volume and the relationship between specific surface area and pore size distribution.

Table 2 Determination of hydrocarbon generation and pore structure parameters of samples

Sample size mg	T °C	Heating rate °C/h	Easy%Ro %	Total gas mL/g	Total oil mg/g	TOC %	S_{BET} m ² /g	V_{BJH} cm ³ /g
797.74	330.0	20	0.55	0.07	2.59	5.51	15.5348	0.027715
813.28	350.1	20	0.64	0.20	5.11	5.11	8.3470	0.022046
749.26	369.8	20	0.72	0.39	8.13	4.81	6.9051	0.021537
796.86	390.3	20	0.83	0.56	9.74	4.63	3.8659	0.020414
800.61	400.5	20	0.89	0.75	10.56	4.43	7.2264	0.030354
699.49	419.9	20	1.07	1.61	10.74	4.22	14.7066	0.050414
649.91	430.8	20	1.17	2.15	8.83	4.01	16.3152	0.050688
801.56	300.0	2	0.56	0.10	3.33	5.56	19.1350	0.031156
798.36	319.9	2	0.65	0.22	5.53	5.17	14.0484	0.027592
799.06	340.0	2	0.75	0.42	8.92	4.82	10.8136	0.024713
799.93	349.9	2	0.80	0.53	10.58	4.54	6.8240	0.022013
800.01	360.0	2	0.86	0.69	11.64	4.37	11.0861	0.031340
700.54	380.3	2	1.04	1.45	12.76	4.27	16.7747	0.043674
495.83	400.1	2	1.26	2.64	7.30	4.16	22.3982	0.052785

Experiment results

Table 2 and Fig. 1 present the hydrocarbon production rate, pore specific surface area, and pore volume test results of the samples at different heating rates.

The gas generation rate of experiment samples continues to rise with the increase of simulated temperature. The corresponding temperature of rapid gas generation is 400.5 °C at 20 °C/h and 360.0 °C at 2 °C/h, which are similar to the maximum generation rate of liquid hydrocarbon. The maximum generation rate of gaseous hydrocarbon is 2.15 mL/g at 430.8 °C at 20 °C/h. The maximum generation

rates of liquid hydrocarbon at two heating rates are 419.9 °C at 20 °C/h and 380.3 °C at 2 °C/h, respectively. With the increase of the simulated temperature, the specific surface area and pore volume of the samples decrease first and then increase. Under the heating rate of 20 °C/h, the BET specific surface area and BJH pore volume reach the lowest at 390.3 °C, while under 2 °C/h, they reach the lowest at 349.9 °C. In terms of the pore structure parameters under the two heating rates, below 349.9 °C, with the increase of temperature, the evolution trend of pore specific surface area and pore volume is similar. When the temperature is higher than 349.9 °C, the pore specific surface area and

Fig. 1 Characteristics of hydrocarbon yield and pore structure change of samples from simulated experiments **a**: total gas; **b**: total oil; **c**: S_{BET} ; **d**: V_{BJH}

pore volume under slow heating conditions are obviously higher than those under rapid heating conditions at the same temperature (Fig. 1).

Discussion

Decrease stage of pore specific surface area and pore volume

During the decrease of pore specific surface area and pore volume (Figs. 2, 3), on the curve at the heating rate of 20 °C/h, it can be seen that with the increase of simulation temperature, the pore volume and specific surface area larger than 10 nm increase as a whole, while pores smaller than 10 nm decrease, especially those with a diameter below 2 nm. On the other hand, when the heating rate is 2 °C/h, the changes of pores with its diameter above 10 nm are less obvious than those at 20 °C/h. But the general trend is similar. It is concluded that the decrease of pores below 10 nm, especially below 2 nm, dominates the decrease of pore specific surface area and pore volume in this evolution stage. Besides, the pore development of the samples is not only affected by temperature, but also by the sedimentary evolution time, mainly for pores over 10 nm.

Increase stage of pore specific surface area and pore volume

During the increase of pore specific surface area and pore volume (Figs. 4, 5), the overall trend for pores with the diameter below 10 nm and between 10 and 100 nm increases with the simulation temperature. For pores greater than 100 nm, there is no obvious rule to follow in its evolution trend. In general, the changes of pores whose diameters are below 100 nm dominate the increase of pore volume in this stage. Combined with the decrease process, it can be seen that within the experiment temperature range of this study, shale pores with the diameter between 10 and 100 nm always increase with the rise of pyrolysis temperature. In other words, it is mainly pores below 10 nm, especially micropores below 2 nm that cause the changes of pore specific surface area and pore volume in Fig. 1c and Fig. 1: first decrease and then increase with the experiment temperature.

Hydrocarbon generation rate and pore structure

From the relationship between hydrocarbon generation rate and pore structure change, it can be seen that there are significant differences in specific surface area and pore volume changes at different heating rates under similar hydrocarbon generation rate. The specific surface area and pore volume at 2 °C/h are obviously larger than those at 20 °C/h during

Fig. 2 Variation of pore structure in the phase of decreasing pore surface area

the decrease stage of specific surface area and pore volume. However, during the increase of specific surface area, there is little difference for those at the two heating rates. It indicates that pore evolution time may be an important factor affecting pore development at this stage. According to the difference between Figs. 2 and 3 pores with a diameter above 10 nm may be the direct cause of this difference. Under similar hydrocarbon generation quantity, the development of corresponding organic pores should be similar from the perspective of organic matter transformation. After comparing the pore structure parameters and hydrocarbon generation quantity at two heating rates in Fig. 6, it is found that when the hydrocarbon generation quantity is similar, the pore structure parameters are quite different. It can be inferred that the formation of this difference mainly comes from the change of inorganic origin pores. Previous studies believe that large volume loss occurred during the process of oil

generation is conducive to the forming of large pores and cracks. But the process of gas generation is conducive to the formation of small cavernous pores (Guo et al. 2020). Meanwhile, some scholars point out that the formation of cavernous organic pores is not only affected by the characteristics of organic matters, but also related to gas expansion (Song et al. 2021). With the increasing simulated temperatures, asphalt and liquid hydrocarbon tend to crack. The devolatilization process of gaseous hydrocarbons leads to the rapid formation and development of organic pores (Milliken et al. 2012), and pyrobitumen is also considered as an important carrier for the development of organic pores (Bernard et al. 2012). As a result, a large number of previous studies have proved that, the organic pores formed in the hydrocarbon generation process of organic-rich shale are mainly micropores, while the inorganic pores are mainly mesopores and macropores (Curtis et al. 2012; Fu et al. 2019; Li et al. 2016;

Fig. 3 Evolution of pore structure in total pore volume reduction stage

Ma et al. 2015). In addition, in this closed experimental system, with the increasing simulated temperatures, the amount of pyrobitumen formed by the cracking of corresponding liquid hydrocarbons will also increase, and resulting in the increasing carrier for the development of organic pores. This also show the increasing degree of development on the corresponding micropores (Mathia et al. 2016). Therefore, the development of organic pores first decreases and then increases with the rise of temperature, which is the core factor affecting the development and evolution of pores in the whole organic-rich shale. For inorganic origin pores, for the sealing degree of the experimental system affects the spatial location of organic matter in shale, and the organic matter filling in inorganic mineral pores has a protective effect on inorganic pores. Thus, these inorganic pores will be released with the continuous consumption of filled organic matter in the stage of higher simulated temperatures (Su et al. 2020). And in addition, the pores increase more with the increase of temperature at a slow heating rate. It be related to the dissolution of minerals by organic acids produced by pyrolysis of organic matter during the evolution of hydrocarbon generation (Cama et al., 2006). Or it may be caused by the crystal structure deformation of mineral components under the combined action of temperature and pressure Fig. 7.

Pore structure evolution characteristics and geological significance

When Easy%Ro is below 0.82%, the pore specific surface area and pore volume decrease with the increase of thermal evolution degree. When Easy%Ro ranges from 0.8 to 1.4%, they increase with the thermal evolution degree. Obviously, there are two possible reasons for the decrease of pore size in the lower evolution stage of organic matters. First, there are fewer primary pores in the original samples, and the pyrolysis productions generated after artificial pyrolysis are stored in these undamaged primary pores. Second, organic matters exist in these primary pores, and the pore space generated by the organic matter consumed by pyrolysis is re-filled by the newly generated pyrolysis products, and there is a possibility of insufficient filling (Sun et al. 2015, 2019; Kuila et al. 2014; Bai et al. 2012). In addition, the difference between the two evolution stages at different heating rates is obvious in specific surface area. A main difference is that the pore specific surface area under the evolution condition with a slower heating rate is slightly higher than that with a more rapid heating rate. It means that rapid settlement may be inconducive to the development of nano-pores under geological conditions. Another difference is that, compared with the specific surface area of pores, the difference of pore

Fig. 4 Variation of pore structure in the stage of increase of total pore surface area

Fig. 5 Variation of pore structure in the stage of total pore volume increase

volume at different heating rates is relatively limited. It indicates that the main factor causing this difference is micropores dominated by organic pores, rather than mesopores and macropores dominated by inorganic pores. Therefore, clarifying the proportion of organic pores under different heating rates will play an important role in the study of oil and gas storage space.

Conclusion

The hydrocarbon generation process of continental shale organic matter is closely related to the evolution of pore structure characteristics. Based on the thermal simulation experiment combined with low temperature physical adsorption experiment under the gold pipe closed system, we obtain the following conclusions:

(1) During the simulation experiment of hydrocarbon generation in continental shale, the specific surface area and

pore volume of nano-pores with the diameter below 10 nm first decrease and then increase with the rise of simulation temperature, while those of pores with the diameter above 10 nm increase all the way. The evolution trend of total specific surface area and pore volume is controlled by pores below 10 nm, especially micropores below 2 nm.

(2) Judging from the relationship between hydrocarbon generation quantity and pore structure parameters at different heating rates, the development of organic pores first decreases and then increases with the rise of temperature, which is the key factor affecting the whole development and evolution trend of pores in the organic-rich shale. On the one hand, the inorganic origin pores are related to the dissolution of minerals by organic acids produced by pyrolysis of organic matter during the evolution of hydrocarbon generation. On the other hand, they may be affected by the crystal structure deformation of mineral components under the combined action of temperature and pressure.

Fig. 6 Relationship between hydrocarbon generation rate and pore structure characteristics

Fig. 7 Thermal evolution and pore structure characteristics

(3) The experimental results demonstrate that rapid settlement under geological conditions is inconducive to the development of nanopores, especially micropores dominated by organic pores.

Acknowledgements This research was supported by the Natural Science Foundation Project of Inner Mongolia (No.2018LH04001), Hondlon District science and technology projects (No.YF2020015), National Natural Science Foundation of China (Grant Nos.:41903060), Natural Science Fund Youth Fund project of Shaanxi Province

(No.2021JQ-953) and Postdoctoral Fund Enterprise Project of Shaanxi province (No.2018BSHQYXMZZ07).

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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