



Research on the Variation Characteristics and Mechanism of the Microstructure of Low-rank Coal under the Action of SC-CO₂

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Abstract: In order to accurately characterize the pore and fracture structure and macromolecular changes of low-rank coal under the action of SC-CO₂, low-rank coal from Shengli No.1 Mine in Xilinhaote, Inner Mongolia was taken as the experimental object. Through an independently built SC-CO₂ immersion experimental system, combined with low-temperature N₂ adsorption, low-temperature CO₂ adsorption and Fourier transform infrared experiments, the changes in the microstructure of low-rank coal before and after SC-CO₂ treatment were analyzed. The results show that: the changes in the pores and fractures of low-rank coal before and after SC-CO₂ treatment promote the transformation of micropores in coal into mesopores, increase the pore volume, and reduce the specific surface area, showing the effects of pore expansion and permeability enhancement, which is conducive to the desorption, diffusion, and seepage of CH₄. The changes in the functional groups of low-rank coal before and after SC-CO₂ treatment show that the peak values of each absorption peak of the coal body decrease to varying degrees, but there is no significant difference in the types of functional groups of the experimental coal samples.

Keywords: SC-CO₂, Low-rank coal, Microstructure.

1. Introduction

As a complex porous medium, the different structures, types, and properties of pores at the micro - scale of coal have a profound impact on the production, migration, adsorption, desorption, and diffusion of coal - bed methane [1], [2], [3], [4], [5], [6]. At present, the exploitation and utilization of coal - bed methane in low - rank coal reservoirs in China are still in the stage of active exploration. The main reason is that the pore structure of low-rank coal seams is complex, and the occurrence of coal - bed methane in low - rank coal is not yet clear. Scholars such as Ju [7] believe that the study of pore structure characteristics, such as pore volume (PV), specific surface area (SSA), pore shape (PS), and pore size distribution (PSD), is the key to revealing the existence of gas [8], [9]. Therefore, in-depth exploration of the pore structure is essential for improving the exploitation efficiency of coal - bed methane in low-rank coal.

Some scholars have studied the changes in the micropore structure of low - rank coal after the action of SC-CO₂. Kaizhong Zhang et al. [10] used the fluid intrusion method for coal samples of different coal ranks and adopted N₂/CO₂ adsorption tests and mercury injection tests to observe the influence law of SC-CO₂ on the pore structures of different coal ranks. The volumes of micropores and mesopores in low - rank (long - flame coal) coal increased. Liu Changjiang et al. [11] conducted SC-CO₂ - H₂O treatment on different coal ranks and found that the proportion of macropores in lignite increased, the changes in transition pores and mesopores were small, and the micropores decreased. The changes in medium - and large - pores of low - rank coal after SC-CO₂ - H₂O treatment were relatively large, and the porosity of lignite increased. Scholars such as Benson B. Gathitu [12] used gas adsorption technology and scanning electron microscopy to study the changes in the pore structure of coal after the action of SC-CO₂ and concluded that the micropore volumes of treated bituminous coal and lignite



both increased. For lignite, the surface areas of mesopores and macropores decreased. Mirzaeian [13] found that the specific surface areas and pore volume distributions of micropores and mesopores of bituminous coal and lignite saturated with SC-CO₂ changed to varying degrees. Regarding the research on the macromolecular structure of low - rank coal, although the action of SC-CO₂ does not change the composition of most oxygen - containing functional groups on the coal surface, it weakens the intensity of their absorption peaks to varying degrees. Wang Tian et al. [14] studied and showed that the action of SC-CO₂ significantly increased the C - O content in lignite and reduced the contents of other oxygen - containing functional groups. The SC-CO₂ reaction improved the parallel orientation degree of coal crystallites in low - rank coal, making the network structure more compact. Sampath et al. [15] directly compared the infrared spectra of lignite and anthracite coal samples before and after the action of SC-CO₂ and found that there were obvious differences in the spectral peak intensities between the saturated and unsaturated coal samples: the absorption peaks of aliphatic hydrocarbon structures, aromatic structures, hydroxyl groups, and oxygen - containing functional groups all decreased to varying degrees. However, the changes in the microstructure after the action of SC-CO₂ still need further research to ensure the exploration and development of deep coal - bed methane resources.

2. Materials and Methods

Experimental Overview

Coal Sample Preparation

The experimental coal samples were collected from the No.5 and No.6 sampling points of Shengli No.1 Mine in Xilinhaote, Inner Mongolia, and the coal type is low - rank coal. The coal samples were collected on - site, sealed with plastic wrap, and then sent to the laboratory. First, the coal samples were processed into coal pillars with a size of $\Phi 25 \times 50$ mm, and the remaining samples were mechanically crushed and ground to prepare 60 - 80 - mesh coal samples. The above two types of coal samples were used as the samples for nuclear magnetic resonance experiments and adsorption experiments, respectively. For the convenience of description, the test samples were numbered according to "coal - coal sample immersion situation". "WH" and "LH" represent the tested No.5 and No.6 low - rank coals respectively, and 0 and 1 represent the raw coal and the coal immersed in SC-CO₂, respectively. For example, "WH - 0" represents the raw coal of No.5 low - rank coal, and the others are in the same way. They were placed in sealed bags and labeled. The analysis was carried out in accordance with "Methods for Proximate Analysis of Coal: GB/T212—2008", and the test results are shown in Table 1 below.

Table 1: Industrial Analysis of Coal Samples Before and After SC-CO₂ Action

Coal Sample	Moisture Content /%	Ash Content /%	Volatile Matter Content /%	True Density /($\text{g} \cdot \text{cm}^{-3}$)
WH-0	30.27	8.14	40.25	1.57
WH-1	30.74	10.04	45.46	1.62
LH-0	18.37	7.43	47.35	1.56
LH-1	18.78	9.24	40.18	1.60

Experimental System

SC-CO₂ Immersion Experiment

An independently developed SC-CO₂ immersion experimental system was adopted. This system consists of two major parts: the SC-CO₂ preparation system and the immersion system. The SC-CO₂ preparation system is mainly divided into the TC - 60 gas booster system and the external CO₂ gas cylinder storage device. The immersion system is composed of a vacuum pumping system and a TMS8023 - 24 precision high - temperature constant - temperature bath. The schematic diagram of the device is shown in Figure 1.





Figure 1: SC-CO₂ Immersion Experimental Device

The coal samples (coal pillars of $\phi 25$ mm \times 50 mm and 60 - 80 - mesh coal powder) were tightly wrapped with cotton and placed in the reaction tank. First, the gas in the tank was evacuated by the vacuum pumping system, and then gas was transported into the tank from the external CO₂ gas cylinder. During this process, a pressure of 10 MPa was applied by the TC-60 gas booster system to change the state of CO₂, and the pressure was kept constant to maintain CO₂ in a supercritical state and transported to the high-pressure gas storage tank for standby. At the same time, a water - bath environment of 45°C was set by the TMS8023-24 precision high-temperature constant-temperature bath. The tank was immersed in the TMS8023-24 precision high-temperature constant - temperature bath, and supercritical CO₂ was transported into the tank to maintain the normal reaction in the tank. After three days of immersion, the experiment ended. The instruments were turned off in sequence, the gas was slowly released, and the samples were carefully taken out and sealed in sealed bags for subsequent experiments.

Low - Temperature N₂ Adsorption Experiment

An ASAP - 2020HD88 research-grade ultra-high - performance fully automatic gas adsorption instrument was used to measure the pore parameters of pores with a diameter greater than 2 nm.

The coal samples before and after SC-CO₂ treatment were degassed in a vacuum at 120°C for 24 h, and a low-temperature N₂ adsorption experiment at 77 K was carried out. The static volumetric method technology was used to obtain high-quality data. The relative pressure of the experiment was set between 0.001 and 0.995. The isothermal adsorption-desorption curve was obtained by changing the pressure, and finally, the curve was analyzed to obtain the pore volume, pore diameter and other data of the coal samples from the low - temperature N₂ adsorption experiment.

Low - Temperature CO₂ Adsorption Experiment

An ASAP-2020HD88 research-grade ultra-high-performance fully automatic gas adsorption instrument was used to test the pores smaller than 2 nm.

The coal samples before and after SC-CO₂ treatment were tested at an experimental temperature of 273 K. The relative pressure was 0.05-0.99. The test principle was similar to that of the low-temperature N₂ experiment. The CO₂ isothermal adsorption curve was obtained by changing different pressure points, and finally, the pore volume and pore diameter data were obtained by analyzing the curve.

Fourier Transform Infrared Spectrometer

Fourier Transform Infrared Spectrometer-Infrared Micro-imaging System VERTEX 70v-HYPERION2000-RAM II, spectral range: 400-15000 cm⁻¹; resolution: 0.5-4 cm⁻¹; signal-to-noise ratio: 40000:1; wavenumber accuracy: 0.01 cm⁻¹; linearity: deviation from 0.0%T < 0.05%T (4 cm⁻¹).



According to the International Union of Pure and Applied Chemistry (IUPAC) [16], pores are divided into micropores: pore diameter < 2 nm; mesopores or intermediate pores: pore diameter 2-50 nm; macropores: pore diameter > 50 nm, and those with a diameter less than 100 nm are called nanopores.

Conclusion

The changes in the pore and fracture structure and functional groups of coal before and after SC-CO₂ immersion were analyzed by combining the low - temperature N₂ adsorption experiment, the low - temperature CO₂ adsorption experiment, and the Fourier transform infrared spectroscopy experiment. The main conclusions are as follows:

After the interaction between SC-CO₂ and coal, since CO₂ molecules enter the pores of coal and have physical or chemical interactions with the coal matrix, some structures of the coal are damaged or reorganized, resulting in an increase in pore space and thus an increase in pore volume. The collapse of some pores is due to the dissolution or migration of certain unstable minerals or organic components in the coal matrix during the reaction with SC-CO₂, causing the pore structure to lose support and thus a reduction in the specific surface area. The changes in the pores and fractures of low-rank coal before and after SC-CO₂ treatment promote the transformation of micropores in coal into mesopores, increase the pore volume, and reduce the specific surface area, showing the effects of pore expansion and permeability enhancement, which is conducive to the desorption, diffusion, and seepage of CH₄.

The changes in the functional groups of low - rank coal before and after SC-CO₂ treatment show that the peak values of each absorption peak of the coal body decrease to varying degrees, but there is no significant difference in the types of functional groups of the experimental coal samples.

Compared with high - rank coal, low - rank coal contains a variety of low - molecular hydrocarbons. Due to its strong dissolution ability, it can be easily extracted and moved by the SC-CO₂ fluid [17]. This not only generates more pore volume but also connects some mesopores in low - rank coal, expanding the mesopore diameter and transforming it into macropores. In addition, affected by the flow of high - pressure SC-CO₂, some organic matter and minerals are washed out of the coal, changing the mineral content and pore morphology.

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