The influence of methane and CO_2 adsorption on the functional groups of coals: Insights from a Fourier transform infrared investigation

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ABSTRACT

Understanding the mechanism of CO_2 and CH_4 storage in coals is critical for CO_2 sequestration in coal seams with enhanced coalbed methane recovery (CO_2-ECBM) and the prevention of mine gas disasters. The primary objective of this study is to investigate the potential chemical interactions of CO_2 and CH_4 with coal due to high-pressure adsorption. The functional groups of two different-rank coals before and after high-pressure CH_4 and CO_2 adsorption treatments were studied using Fourier transform infrared spectroscopy (FTIR) spectrometry and curve fitting. The changes in the chemical structure of coal were evaluated using structural parameters derived from FTIR. The coal adsorption treatments were conducted at 40 °C and 6 MPa. The results indicate that both coal rank samples underwent functional group and structural parameter changes after high-pressure CO_2 and supercritical CH_4 adsorption and thus that chemical interactions occur at high pressure. Moreover, the variation law of functional groups is complex due to its dependence on the coal rank and gas type. FTIR spectra of long-flame coal and anthracite coal have clear functional group distribution differences. The amount of oxygen-containing functional groups decreases with the increase in coal rank. This study demonstrates the utility of FTIR spectrometry and curve fitting to quantitatively evaluate the chemical structure of coal samples. This preliminary study is intended to enrich the theories of gas adsorption in coals, guide applications of CO_2-ECBM, and assist in the prevention of mine gas disasters.

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1. Introduction

Recently, CO_2-enhanced coalbed methane (CO_2-ECBM) production has become a priority in academic research to alleviate the global greenhouse effect caused by excessive emissions of CO_2. Injecting carbon dioxide into coalbed reservoirs improves the recovery of coalbed methane (CBM) and simultaneously sequesters CO_2 in coal seams (Mares et al., 2009; Orr, 2009). In addition, increasing the mining depth further significantly increases the gas content of coal seams and leads to more severe gas disasters. Numerous coal mines in multiple countries, including China, Australia, Czech, France, Poland and Turkey, contain large quantities of CO_2, associated with a tendency for large coal and carbon dioxide outbursts (Beamish and Crosdale, 1998; Karacan, 2007; Li et al., 2011). Thus, research on the storage and flow mechanism of CH_4 and CO_2 in coals is intended to promote the prevention and control of gas disasters in coal mining, exploitation and utilization of methane resources, and geological sequestration of carbon dioxide. To date, there have been numerous studies concerning the adsorption-desorption behavior of methane and CO_2 on coals (Clarkson and Bustin, 2000; Mastalerz et al., 2004; Zhang et al., 2011), displacement of coalbed methane recovered by CO_2 injection (Prusty, 2008; Zhou et al., 2013), and coal matrix swelling induced by methane and CO_2 adsorption (Day et al., 2011; Mazumder and Wolf, 2008; Pan and Connell, 2011; Shi et al., 2014; Wang et al., 2017a). However, little is known about the potential chemical and structural changes of coal in response to CO_2 and CH_4 adsorption under specific temperature and pressure conditions. This issue remains controversial.

Goodman et al. (2005) showed that no chemical reactions occur

between injected CO_2 and oxygenated functional groups during CO_2 sorption on coals, which supports the physical process of adsorption. Based on high-pressure static and dynamic experiments on coals, Mazumder et al. (2006) determined that although no direct evidence shows that coals react during the adsorption process, the occurrence of reactions cannot be ruled out. Some scholars (Kolak and Burruss, 2006, 2014; Kolak et al., 2015; Zhang et al., 2013) have found that during CO_2 injection, certain alkanes and polycyclic aromatic hydrocarbons (PAHs) were liberated and mobilized in coal, indicating that chemical interactions took place. Mastalerz et al. (2010, 2012) compared the functional group distribution of coal lithotypes before and after CO_2 injection at high pressure using FTIR techniques. The results showed no changes in functional groups, supporting physical CO_2 sorption. The results also indicated that minor molecular changes occurred in the coals and that those changes could not be detected by FTIR techniques. Cao et al. (2011) investigated whether there were any chemical changes in coals from CO_2 adsorption using advanced solid-state 13C NMR techniques. Their studies suggested that injected CO_2 chemically interacted with coals. Wang et al. (2015, 2016) used FTIR analysis to analyze the surface chemistry of various coals. They found less oxygen-containing functional groups in coals exposed to CO_2 relative to that of raw samples, which is likely due to chemical reactions between supercritical CO_2 fluid and coals. Despite these studies, the issue of whether CO_2 adsorption on coal is purely a physical process or a combination of physical and chemical reactions remains unclear.

Most scholars have concluded that the interaction between coal and CH_4 consists of physical adsorption (Liu et al., 2013; Moffat and Weale, 1955; Rubes et al., 2010; Saunders et al., 1985; Xiang et al., 2014). The essence of the interaction is the result of mutual attraction between gas molecules and molecules on the coal surface through Van der Waals forces. However, most conclusions are from low-pressure adsorption studies. Research on the potential chemical reactions of high-pressure CH_4 (such as supercritical methane) with coal are scarce. Most scholars investigate the interactions between methane and coal by calculating the adsorption heat or adsorption potential based on molecular simulations. FTIR spectroscopy has only rarely been applied to evaluate changes in the chemical structure of coals during methane adsorption. Moreover, there remain disagreements about the mechanism of methane adsorption on coal. An experimental study of Majewska et al. (2010) showed that methane adsorption can alter the chemical structure of coal. Goodman et al. (2006) and Larsen (2004) concluded that coal swelling induced by the adsorption of CO_2, CH_4, and other molecules is irreversible, possibly due to molecular rearrangement in the coals and a loss of molecular rigidity during interactions between coal and CH_4, CO_2, and H_2O molecules. Zhang (1990) and Zhang et al. (2005) indicated that CH_4 sorption on coals is both a physical adsorption (or physisorption) process and a chemisorption process. However, they did not present supporting evidence for this hypothesis. Therefore, to clearly understand the mechanism of methane adsorption on coal, further studies are required.

As one of the most powerful, versatile, non-destructive analytical techniques, Fourier transform infrared spectroscopy (FTIR) is an effective method for characterizing the chemical structure of geological samples, such as coal (Ahmed, 2003; Chen et al., 2015; Iglesias et al., 1995; Mastalerz and Bustin, 1996; Wang et al., 2017b), shale (Gasaway et al., 2017; Lis et al., 2005), silicate glass (Ibrahim et al., 2016; Von Aulock et al., 2014) and minerals (Rossman, 2006). The functional groups in the complex macromolecular structures of coals can be studied by infrared spectroscopy (Li et al., 2016; Painter et al., 1987). In this study, we used Fourier transform infrared spectroscopy (FTIR) techniques to (i)

investigate the differences in the chemical structures of two different-rank coals and (ii) determine possible changes in the functional groups of the coals after high-pressure CH_4 and CO_2 adsorption treatments.

2. Experimental methods

2.1. Sample materials

Two different-rank coals from different mines in China were collected: a long-flame coal from Henan Province (HN) and an anthracite coal from Shanxi province (SX). The coal samples were preserved in sealed plastic bags filled with helium (He) to prevent undesired physical and chemical changes due to atmospheric oxidation. The raw coal samples (air-dried basis) were crushed to 200 mesh (74 μm). Proximate analyses (ash, volatile matter, and fixed carbon) were performed using a proximate analyzer (GF-A2000, China) according to the China's National Standard GB/T 212-2008. Ultimate analyses (carbon, hydrogen, nitrogen, and sulfur) were performed using an elemental analyzer (Vario EL cube, Germany), and the oxygen content was calculated from the difference. The basic parameters are shown in Table 1.

2.2. High-pressure adsorption treatments

2.2.1. Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1, in which 'PG' represents the pressure gauge, 'VG' represents the vacuum gauge, 'V' represents the valve, 'PGV' represents the pressure gauge valve, 'VGV' represents the vacuum gauge valve, 'VV' represents the vacuum valve, 'RCV' represents the reference cell valve, 'SCV1' represents the sample cell-1 valve, and 'SCV2' represents the sample cell-2 valve. The gas is filled from the left side of the pipeline by adjusting valve V1. The sample cells were submerged in water, and the water temperature was controlled to keep the cells at a constant temperature. The water bath also assisted in detecting the air-tightness of the experimental system (Wang et al., 2014).

2.2.2. Air-tightness detection

The air-tightness of the experimental system is crucial for accurate measurements. Before each experiment, the air-tightness of the apparatus was checked. After the system was assembled, VV, V1, and V5 were closed, and other valves were kept open. Pure helium (He) was injected into the system by opening V1. If no bubbles escaped from the sample cells, the connections submerged in the water bath were airtight. The air-tightness of the connections in the air was confirmed by monitoring the pressure gauges. If the pressure gauge readings were constant for 24 h, the system was considered airtight.

2.2.3. Adsorption treatment measurements

The experimental procedures are as follows:

(1) Approximately 120 g of coal samples were weighed and split into two equal amounts. The two parts were quickly separated into

Table 1
Selected parameters of the raw coals.

Sample	M_{ad}(%)	A_{ad}(%)	V_{daf}(%)	FC_{ad}(%)	C	H	N	S	O*
HN	10.39	3.24	39.47	46.9	78.12	6.26	1.53	0.45	13.64
SX	0.7	13.33	10.29	75.75	86.33	3.43	0.76	0.31	9.17

M_{ad}—moisture content on air-dried basis, A_{ad}—ash content on dry basis, V_{daf}—volatile matter content on dry-ash-free basis, FC_{ad}—Fixed carbon, * by difference.