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Characterization of coalification jumps during high rank coal chemical structure evolution

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HIGHLIGHTS

- A new coalification jump was identified at $R_{o,max}$ (3.22–3.03%).
- Structural parameters of the macromolecular structure of vitrinite are proposed.
- Structural evolution in high coal rank was characterized by FTIR.

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ABSTRACT

The functional groups and coalification jumps were studied by the Fourier Transform Infrared spectroscopy (FTIR), characterized along with the increasing temperature. The raw coal sample with high coal rank ($R_{o,max}$ = 1.82%) was used to further form some high rank samples using improved microscale sealed vessel (MSSV) pyrolysis method for the FTIR analyses. The MSSV pyrolysis simulates coalification process under different temperatures by heating the raw coal from 350 °C to 550 °C at a heating rate of 10 °C/h, producing the high rank coal samples that can be used for characterization of the functional groups and coalification jumps. Combined with proximate and ultimate analyses, FTIR provides new insight to the chemical structure of the coal samples. The results show that the typical vibration of function groups includes C—H aromatic out-of-plane deformation at 877 cm^{-1}, 812 cm^{-1} and 784 cm^{-1}; carbonyl/carboxyl C=O stretching at 1712 cm^{-1}; —OH stretching at 3422 cm^{-1} and aromatic C—H stretching at 3040 cm^{-1}. The structural parameters, such as degree of condensation 1 and 2 (DOC1, DOC2), aromaticity 1 and 2 (AR1, AR2), A-factor, C-factor, and CH_2/CH_3 were calculated by peaks area of the FTIR spectrum. The calculation provides fundamental information to correlate the intensity of functional groups factors such as temperature and vitrinite reflectance etc. It was found that AR2 values for semi-anthracites and anthracites showed relatively large variation, likely because of the decreasing intensities of Char peaks via de-functionalization during coalification. Besides, AR1 and AR2 behave quite similarly as their FTIR spectrum peaks show the same range from 450 °C to 500 °C. The values of both DOC1 and DOC2 generally increased in the range of temperature from 350 °C to 370 °C and reached the peak at 370 °C followed by a sharp decline. The phenomenon was likely due to the large loss of hydrogen in corresponding temperature range, which limited intensities of the aromatic CH_x stretching band at 3000–3100 cm^{-1}. The A-factor and C-factor gradually decreased as temperature increased. In addition, the jumps were presented in terms of the structural parameters and methane yield lines. A new jump was identified at $R_{o,max}$ = 3.22–3.03% after 470 °C. Furthermore the methane yield data comparatively show consistent with the functional group of vitrinite molecule in different rank.

1. Introduction

During coalification, the organic structure of coal consisting of heterogeneous aromatic compounds keep changing with aromaticity increasing from low rank to high rank coals [1]. The most commonly used parameter to describe the coal maturity is vitrinite reflectance [2]. Vitrinite reflectance, corresponding to coal rank,

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is recognized to monitor the maturation of organic matter. Moreover, kinetics of vitrinite reflectance can be used to analyze different vitrinite reflectance evolutions with heating time at various conditions [3]. The Fourier Transform Infrared (FTIR) spectra of kerogens with increasing maturity can be used to characterize different results, exhibiting increasing aromatic absorption, decreasing aliphatic absorption and decreasing carbonyl and carboxyl absorption [4]. Many studies reveal there might exist four or five jumps during the coal structural evolution process. Some characteristics of coal, e.g. the yields of soluble organic matter were changing significantly along with coal maturity. These yields increase up to a maximum with coal maturity close to $R_{o,max}$ = 0.9%, and a notably rapid decrease occurs when $R_{o,max}$ is approximately 1.4% [5]. As the coal maturity increases, its chemical composition and structural characteristics during the coalification would be controlled by coal molecular structure.

FTIR can be used to analyze carboxyl group and coal aromaticity and main structural changes that take place during coalification [6,7]. For instance, FTIR has been used to study structural differences of xylite and matrix lignite in coal [1]. It is also widely used to investigate the chemical functional groups in macerals across different coal ranks, especially for those of $R_{o,max}$ lower than 2.0%. Some intense and stable absorbance peaks or area ratios, including aromaticity, degree of aromatic ring condensation, chain length and A, C factors, were presented well with reflectance micro-FTIR [8,9]. In order to further examine the structural modifications of coal, the elemental analysis, structural parameters and COOH group analysis have been used to resolve evolution of aliphatic structures and aromatic structures. However, only few studies dealt with structural parameters of coal with different maturity ($R_{o,max}$ > 5.0%), and only four jumps during coalification have been reported in open literature, referring to the discussion as follow. In addition, Most of the FTIR data reported in literature so far were focused on low rank, very little on high rank in previous studies. For low rank and higher-rank coals, some structural parameters of coal show obvious increasing or decreasing with coal maturity. Aromaticity 1 (AR1), Aromaticity 2 (AR2) and CH_2/CH_3 ratio show a good linear relationship with vitrinite reflectance when $R_{o,max}$ < 1.3%, corresponding to the second jump during coalification [8]. However, the data associated with the coal with $R_{o,max}$ > 2.5% are incomplete. Thus, FTIR measurements with more samples under laboratory conditions should be considered especially.

Meanwhile, FTIR can be used to determine the functional groups of coal as well, e.g. aliphatic and aromatic carbon, oxygen functional group [10]. Previous results demonstrate that degree of substitution rapidly decreased in the early stage of coalification, and large aromatic clusters in semi-anthracite and anthracite, and an average aromatic ring size of 3 to 4 or more can be identified by ^{13}C NMR analysis for highly matured coal [11]. The structural parameters, which allow the analysis of types and apparent aromaticity, show the same characteristic of the change with functional groups [12]. It has been reported based on FTIR study using coals from the Bowen Basin of Australia, the FTIR value was well correlated to the vitrinite reflectance, which can be applied to characterize coal macerals, in particular telocollinite, and can be further used to investigate changes in the aromatic and aliphatic functional groups in the telocollinite, over a wide rank range ($R_{o,max}$ = 0.39–3.52%) [13].

While a considerable amount of research has been focused on characterization and quantitative structural investigation of coals ranging from peat to semi-anthracite using FTIR, few studies can be found to deal with the structural evolution in high coal rank, especially where all the samples come from one coal by thermal simulation. In this work, a series of coal samples thermally formed from one collected coal were obtained with different vitrinite reflectance of more than 1.82%, which can make all the samples have been composed of the same components and all the samples were not affected by other geological factors. These samples were investigated by FTIR. This provides a large amount of experimental information for calculation of various structural parameters of coals. Thus the FTIR values can be correlated to a wider range of the geological factors. As a result, the relationship between FTIR values and the temperature and vitrinite reflectance has been systematical investigated, providing the better understanding of coalification jumps during high rank coal chemical structure evolution.

2. Materials and methods

2.1. Samples and preparation

The coal sampling area is located at the Permo-Carboniferous Xingtai Coalfield in North China plate. The coal sample was collected from the Xiandewang (XDW) Mine located in the southern part of the Xingtai Coalfield. One bench sample of meagre coal was obtained from the surface of the No. 1 coal seam at Xiandewang Mine above, following the Chinese standard method (GB/T 482-2008) [14]. The sampling position is located in the mining face, where the surface elevation is 600 m below sea level and there are no apparent geological structural faults and magmatite. The size of the coal bench sample is 20 cm × 20 cm × 10 cm. All collected samples were immediately placed in a polyethylene bag filled with nitrogen gas to minimize oxidation and contamination. The method used for vitrinite sample separating from coal is the same as the previous study reported by Li et al. [9]. High purity vitrinite was obtained. Vitrinite reflectance was measured following the Chinese national standard issued in 2008 (GB/T 6948-2008) [15].

As coal was composed of mixtures of various macerals, the evolution of molecular structure of macerals with different components had a significant difference with respect to hydrocarbon generation. Thus, a series of coal samples with different maturity, one sample of 11 solid vitrinite samples was taken and others were collected from the vitrinite sample by the pyrolysis under different temperature can provide a better understanding of hydrocarbon generation mechanism in coalification.

A closed-system pyrolysis using improved microscale sealed vessel (MSSV) was applied for the vitrinite pyrolysis experiment. The experiment includes three parts. Firstly, 10 mg of vitrinite and a little silica wool were placed in a preparative glass tube and then the tube was sealed. Secondly, 10 vacuum glass tubes made from the first step were placed in a pyrolysis apparatus connecting to power with temperature-programmed heating at a heating rate of 10 °C/h. Finally, the samples were removed from the pyrolysis apparatus at a pre-set temperature for further processing. The final solid products were collected by a plastic bottle to provide samples for analysis of the vitrinite structure.

2.2. FTIR spectroscopy

Powdered sample (namely with XDW) was heated from room temperature to 550 °C at a heating rate of 10 °C/h. The total 11 solid samples including one vitrinite sample (XDW) and ten residue vitrinite samples collected by the pyrolysis were chosen for FTIR spectra measurements. The ten residue vitrinite samples were named by prefixion XDW plus "temperature", in which the temperature is started from 350 °C until 530 °C at an interval of 20 °C, such as XDW-350 and XDW-370. All FTIR measurements were performed in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, with an absorbance model using