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The role of structure defects in the deformation of anthracite and their influence on the macromolecular structure

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HIGHLIGHTS

- The correlation between structure defects and deformation was established.
- The role of SW defect in the deformation of anthracite was studied by calculation.
- The SW defect reduces the energy needed to produce CO gas from anthracite.

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ABSTRACT

The impacts of stress on the physical and optical properties of coals are well recognized, while the influence on the chemical structure is seldom considered. In the light of mechanochemistry research that mechanical force can act on the molecule directly to initiate or accelerate reactions by deforming the chemical bonds, it is meaningful to consider how stress works on the macromolecule of coals. In this work, some insights are given based on anthracites with different tectonic deformation from Qinshui Basin, Shanxi Province, China. The deformation degree was measured by bireflectance ($R_{o,max} - R_{o,min}$), and the macromolecular structure was characterized by Raman spectroscopy. For samples from the same colliery, there is a positive relationship between Raman area ratio A_D/A_G and bireflectance, suggesting that the deformation of anthracite is related with the generation of structure defects at the atomic scale. Further quantum chemistry calculations demonstrate that accompanying the generation of one Stone-Wales (SW) defect (induced via in-plane rotation of C-C bond by 90°), the molecular geometries of anthracite, such as chemical bonds and angles, change. The deviation of atoms from their equilibrium geometries reflects the local force distribution and transfers 303.48 kJ/mol mechanical energy into chemical energy. These changes allow chemical bonds to adjust to the applied stress without breakage, so that anthracite will accommodate plastic deformation. Additionally, the existence of SW defect slightly reduces the energy needed to produce carbon monoxide from carbonyl in anthracite. The current study helps to understand the potential influence of stress on the chemical structure evolution of coals.

1. Introduction

The chemical structure evolution of coals is the foundation for understanding coalification and the accompanying volatile [1] and possible oil generation [2]. These chemical transformations are generally thought to be influenced by, like any chemical reaction, temperature [3], time [4], pressure [5], and possible catalysis [6]. Most researchers recognize that stress, which occurs extensively in geology, can impact the physical [7–9] and optical [10,11] structure of coals and do not consider its possible influence on the chemical structure. Recent years have seen a breakthrough in the single molecule mechanochemistry, which proves that stress can act on the molecule directly to initiate or accelerate reactions by deforming the chemical bonds [12–15]. This background provides incentive to further explore the possible impacts of stress on the chemical structure of coals. Xu et al. [16] suggested that the bond breakage in anthracite during deformation experiments could result in gas generation. Liu et al. [17,18], in a comprehensive study of the chemical properties of superfine pulverized coal

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particles, considered that the mechanochemical effect during the coal comminution resulted in the free radicals and carbon structure variations. Coal is a complex macromolecular compound and does not possess a definite chemical structure. Researchers have proposed lots of macromolecular models to represent the chemical structural features of coals [19]. But information concerning how stress works on the macromolecular structure is limited.

To determine the macromolecular structure response of coals under stress, in our previous study, we performed deformation experiments on anthracite [20]. Results revealed that when stress was favorable in facilitating structure defect generation, anthracite would accommodate more strain and exhibited as ductile deformation when fractured. If anthracite is deformed by the generation of structure defects at the atomic scale as we preliminarily proposed, by studying the influence of structure defects we can better obtain the influence of stress upon the chemical structure of coals. Although the deformation experiment provides some interesting insights, there were only three ductile deformed samples. More evidence is needed to examine the relationship between structure defects and deformation.

In this study, using a series of tectonically deformed anthracites from Qinshui Basin, Shanxi Province, China, we continue to investigate the relation between structure defects and deformation. Structure defects are revealed by Raman spectroscopy, which is a widely-used method to characterize structure defects in carbonaceous materials [21–25]. The deformation degree is measured by vitrinite reflectance anisotropy parameter bireflectance (=$R_{o,max} - R_{o,min}$), which is mainly a product of stress or strain in deformed areas [26,27]. Experiment research indicated that samples with a higher strain tended to have a greater bireflectance when deformed at the same temperature [28]. The role of structure defects and their influence on the macromolecule are further discussed using quantum chemistry calculations.

2. Geological setting and sampling

Samples were collected from Wangtaipu Colliery and Sihe Colliery in the Qinshui Basin, Shanxi Province, China. Wangtaipu Colliery is in the eastern margin of Qinshui basin (Fig. 1a). The main coal-bearing strata in Wangtaipu Colliery range from Carboniferous to Permian, which strike NE and dip NW with an angle of 4–5°. Coal seam No. 15 in the lower Taiyuan Formation of the Upper Carboniferous is the main minable coal seam in the XV5306 working face. Normal fault DF133 and a nearby normal fault (here we name it DF133′) are found in the north-eastern of the working face (Fig. 1b). DF133 strikes 97°, dips 7° with an angle of 80°, and DF133′ strikes 84°, dips 354° with an angle of 80°. They both have a stratigraphic displacement of 1.6 m. Wangtaipu samples were collected near faults DF133 and DF133′. Sihe Colliery is in the south-eastern Qinshui Basin (Fig. 1a). Coal seam No. 3 in the Shanxi Formation of the Lower Permian is the main minable seam. The structure characteristics of the W2301 working face are mainly controlled by the anticline in the west and the reverse fault DF9 in the east (Fig. 1c). The DF9 has a stratigraphic displacement of 6 m and dips 265° with an angle of 15–35°. Sihe samples were collected from these two local deformed regions. Samples from the anticline are named by S-Z, and from the DF9 are named by S-D. General information of the samples is summarized in Table 1.

Collected samples are quite soft and can be broken easily by hand (Fig. 2). Primary structures, such as the bedding plane, in most samples were damaged. Instead, tectonically induced features, such as friction surfaces, crumple, and exogenous fractures can be observed in these tectonically deformed coals (Fig. 2).

3. Methods

3.1. Vitrinite reflectance

Due to low strength of deformed coals, it is difficult to make oriented samples. Therefore, reflectance measurements were performed on polished grain blocks using the Zeiss Axio Imager M1m photometer microscope with reflected, monochromatic, and polarized light (oil immersion) in Henan Polytechnic University. After calibrating the photometric system, vitrinite reflectance were continuously measured as the stage was rotated through 360°. At each measurement point, an apparent maximum reflectance ($R'max$) and an apparent minimum reflectance ($R'min$) were recorded. About 200 measurement points were selected on one specimen, usually on banded telocollinite. On the basis of collected data, the maximum ($R_{o,max}$) and minimum vitrinite reflectance values ($R_{o,min}$) were calculated using Kilby's method [29] and Duber's improvement [30]. The calculations details can be found in Supplementary Material I.

3.2. Raman spectroscopy and spectra analysis

Raman spectra of the samples were examined in-situ by a Jobin Yvon HR640 instrument with microscopy, equipped with 50× objective in Tsinghua University. A 532 nm Nd-YAG laser was used as the illumination source. The laser power was controlled to 2.5 mW to avoid thermal alteration of the sample. Spectra were collected at room temperature for 10 s over the spectral range of 700–2200 cm^{-1}, covering the first-order region (1000–1800 cm^{-1}). Considering the heterogeneity of coal, for each sample Raman spectra were collected from three different locations.

4. Results

4.1. Vitrinite reflectance and bireflectance

4.1.1. Wangtaipu samples

Samples from Wangtaipu Colliery are of similar $R_{o,max}$ (4.3%), which fall into the category of anthracite B according to ISO11760 (Classification of coals). The Fig. 3a reveals that there is a negative correlation between $R_{o,min}$ and bireflectance. The increase of bireflectance with the decrease of $R_{o,min}$ is viewed as the beginning of pre-graphitization, which usually occurs at $R_{o,max} > 6.0\%$ [31]. The early pre-graphitization can be attributed to the influence of stress (or strain) as suggested by Wilks et al. [28] and Bustin et al. [32]. Sample W-2 is of the highest bireflectance, which also shows obvious tectonic stress influence, in that it was deformed into powder coal. On the contrary, sample W-1 with the lowest bireflectance, though exhibiting some fractures, still possesses the bedding plane, indicating a weaker influence of the tectonic stress. Sample W-3 is the medium, both in bireflectance and the macroscopic damaging features, as the bedding plane is folded and exogenetic fractures are well developed.

4.1.2. Sihe samples

The $R_{o,max}$ values of Sihe samples range from 3.00 to 4.32%, which are mainly anthracite C (according to ISO11760), except that sample S-D-4 ($R_{o,max} = 4.32\%$) is the anthracite B. According to Fig. 1 the burial of anticline is about 15 m deeper than the reverse fault, so if $R_{o,max}$ is only influenced by temperature, $R_{o,max}$ values of S-Z samples should be similar or a little higher than S-D samples. However, there is no such a relation, indicating that $R_{o,max}$ values are also influenced by tectonic stress. The $R_{o,min}$ and bireflectance values vary from 2.27 to 3.35% and 0.73 to 1.12%, respectively. The Fig. 3b indicates that both $R_{o,min}$ and bireflectance show a good