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Chemical structural transformations of different coal components at the similar coal rank by HRTEM in situ heating

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ABSTRACT

The structural transformations in three coal components, barkinite, vitrinite and resinite, on heat-treatment from 200 to 700 °C were investigated by high-resolution transmission electron microscopy (HRTEM) technique. The orientation in chemical structure was examined by HRTEM image. The orientation in aromatic layers of three coal components increased gradually on heating from 200 °C to 700 °C. Vitrinite followed barkinite's transition some 50 °C later in temperatures of chemical structural change than barkinite. The transformations of structural parameters derived from TEM images of three coal components were different, including the interlayer spacing (d), the layer size (La), the number of aromatic layers per stack (n), and the aromatic layer stacking height (Lc). At least three temperature stages (200–400, 400–600, and 600–700 °C) were shown. Barkinite has similar change trends of d, Lc, and n with resinite however the La values were similar to vitrinite at 200–700 °C. Both barkinite and resinite had significant decreased d values at 200–400 °C and gradual decreased from 400 °C to 600 °C. The values of Lc and n for barkinite and resinite exhibit no obvious changes at 200–400 °C and increased significantly > 450 °C. Vitrinite decrease significantly in d from 450 to 600 °C (4.32–3.62 Å) and increase greatly in Lc and d up to 450 °C (12.84–20.29 Å). Vitrinite and barkinite have two temperature ranges for increasing significantly in La from 400 °C to 700 °C. When the temperature is > 600 °C, these coal components had much larger Lc, n, and La values with temperature increasing and decreased gradually in d values. The variation of structural parameters when heating was explained by the alteration of chemical structures in coal on pyrolysis and plastic behavior.

1. Introduction

Coal complexity and diversity in behavior within and between coals is related to rank and the maceral compositional differences [1]. The macerals can behavior differently upon heating [1,2]. In general, the aliphatic fraction is gradually removed while the aromatic materials coalesce into larger clusters [2] during coalification process. The orientation is increased and seems parallel to the bedding planes based on HRTEM [2]. The structural changes on heating influences coal utilization: gasification, combustion, and liquefaction. So, a fundamental understanding of the transformation of coal on heat-treatment is desirable.

The structural transformations of coal when heated have been studied using optical properties (reflectivity of vitrinite) [3], FTIR [4,5], X-ray diffraction (XRD) [5–11], and high resolution transmission electron microscopy (HRTEM) [12–16]. XRD and FTIR techniques were frequently applied in the previous works, but HRTEM method has the advantage of providing a visual structural insight into the transformations rather than a simple numeric. Evans et al. [15] studied the layer diameter length of heat-treated coals from XRD and HRTEM techniques. Davis et al. [16] discussed the average fringe lengths and relative amounts of crystalline structure of combusted-coal chars using HRTEM micrographs. There has been considerable progress in obtaining quantitative data from HRTEM micrographs. Sharma et al. [12] developed a new filtration technique for HRTEM images and applied this method to show a remarkable structural change during coal gasification. Sharma et al. [14] evaluated the stacking number and layer size of heat-treated coals. The structural changes were highly dependent on whether a coal undergoes a plastic stage. A direct measure of the orientation covering the rank range of lignite to anthracite by HRTEM was studied [17–21]. Most of the work discussed was based on image analysis of the lattice fringe micrographs that are extraction from the original micrograph by image processing techniques [12–14,22–24].

Vitrinite or coal on the concentration of vitrinite, in the past works, is often used to discuss the coal structural transformation with heat-

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treatment. Little information on the other coal macerals, especially liptinitic maceral, was studied. Meanwhile, the samples observed by HRTEM are from the products of different coal technologies, such as coal char [12], not directly coal components. Furthermore, the changes in chemical structure of coal components by HRTEM in situ with heating procedure were rarely reported. HRTEM in situ heat-treatment would have a significant advantage over HRTEM is that it can provide directly image-observed in different temperature stages.

Vitrinite and resinite were termed as coal macerals by the International Committee for Coal and Organic Petrology (ICCP) organization and they were widely accepted. However, barkinite has not been recognized as a coal maceral by ICCP organization although barkinite has special petrological characteristics [25–28]. Barkinite is considered to derive from the cortex tissue of stem and root of plants in which the cell wall and filling material apparently have become impregnated with suberin substances [29]. The major question is that unclear chemical structure of barkinite, as pointed out by Hower et al. [30], particularly the changes in structure on heating.

Here, the structural transformations of vitrinite, barkinite and resinite with heat-treatment by HRTEM with in situ heating procedure, and the structural parameter changes of these three coal components with different temperatures are discussed.

2. Experimental

2.1. Samples selection

Barkinite and vitrinite were from the same coal sample, which was selected from B_3 coal seam in Mingshan mine, Jiangxi province, P.R. China. Resinite was separated by hand picking from Fushun coal, Liaoning province. Barkinite and vitrinite were separately first by hand picking. Vitrain band was selected to obtain pure vitrinite, and durain band for barkinite. The samples were crushed to −18 mesh to make pellets for determining maceral compositions. Petrographic analysis showed that bright bands were 87% vitrinite and the dull bands were 83% barkinite. Thus, for pure barkinite and vitrinite separated by density gradient centrifugation (DGC) method. The detailed procedure for maceral separation was described in the work of Guo et al. [31]. The purities of barkinite-separated (BaS) and vitrinite-separated (VS) were above 95% (Vol.%), and that of resinite was also up to 98% (Vol.%), as listed in Table 1. The vitrinite reflectances (R_o) were determined by a Zeiss Universal reflected-light microscope fitted with a 40X-oil-immersion objective and 10X ocular lenses. Reflectance reported was the mean value of 100 measurements. The values of average maximum vitrinite reflectance of the samples used are also shown in Table 1. The R_o values of barkinite and vitrinite are 0.21% and 0.69%, separately. The R_o of resinite was not determined, but the R_o value of Fushun coal is 0.56%.

2.2. HRTEM observation

HRTEM observations were performed on a 200 kV transmission electron microscope (JEOL, JEM-2010) with a heating system (electric furnace). For each test, sample was first diluted with ethanol and sonificated for 20 min to disperse the particles. Sample was sprayed over a silicon nitride film. Individual particles were first examined at moderate magnification to find the particle with thin sharp edges and such region were then magnified to observe lattice fringes. The samples were heated in situ from the temperature range of 200–700 °C for observing their structural changes with increase of temperatures used. The temperatures at 200–700 °C were chosen owing to the limitation of heating instrument used. The temperature desired was controlled using the conversion of thermo electromotive force and temperature. In the present study, the detailed HRTEM acquisition method proposed by Sharma et al. [13] was used.

In this study, some parameters derived from HRTEM were used to discuss the chemical structural changes with heat-treatment, including the interlayer spacing (d), the layer size (La), the number of aromatic layers per stack (n), and the aromatic layer stacking height (Lc). To obtain quantitative information of these parameters, the lattice fringe images were subjected to the image analysis. The distributions are the average of the distributions obtained from at least 10–15 fields for each sample.

3. Results and discussion

3.1. Orientation changes with different temperatures

The HRTEM micrographs of BaS and VS were observed and further converted to lattice fringe images. HRTEM images and corresponding lattice fringe images of barkinite, vitrinite, and resinite with different temperatures are shown Figs. 1–3, separately. For barkinite, at 200 °C, poor orientation was shown (Fig. 1(a, b)). With increased temperature to 250 °C, a clear orientation in some parts of coal particle was observed (Fig. 1(c, d)). Some lattice fringes show parallel to each other. Fig. 1(e, f) show that most of layers were orientated at 300 °C. After this temperature, the orientation of layers increased until to 400 °C. This will continue to 550 °C and more stacking increased. Layers start aligning at 550 °C and become highly orientated and more stacking from 600 to 700 °C.

A similar result, for vitrinite, of orientation changes in chemical structure when heating from 200 to 700 °C was observed (Fig. 2). The orientation increased gradually and the degree of aromatic layers condensation became obvious. However, the change temperatures of vitrinite are often later 50 °C than that of barkinite. Namely, for vitrinite, most of layers are orientated at 350 °C, more stacks are formed at 450 °C, and become aligning at 600 °C.

At the beginning temperature of 200 °C, resinite showed parts of orientation in chemical structure, especially at the edge of coal particle (Fig. 3). With the increasing of temperature, the orientation of chemical structure and the degree of aromatization increased gradually. But it should be pointed out that it is difficult to find a certain thin sample site for observing at the whole temperature ranges used owing to the flow of resinite on heating.

Table 1
Basic information and some temperatures of thermal behaviors.

Coal ID#	R_o (%)	Vitrinite content (Vol.%)	Barkinite content (Vol.%)	Resinite content (Vol.%)	T_{max} (°C)	T_s (°C)	MFT (°C)	T_r (°C)
LP [38]	0.69	24.3	62.9	–	424	407	441	481
LP-2 [38]	0.73	64.5	19.9	–	411	390	443	484
LP-4 [38]	0.67	15.0	80.6	–	415	412	436	–
Barkinite [39]	0.21	< 3.0	> 95.0	–	454	–	–	–
Vitrinite [39]	0.69	> 95.0	0.0	–	453	–	–	–
Resinite	–	–	–	> 98.0	–	–	–	–

R_o, the average maximum vitrinite reflectance (expect barkinite); T_{max}, temperature of the maximum volatile matter loss; T_s, softening temperature; MFT, the temperature of maximum fluidity; T_r, resolidification temperature; –, no data.