STRUCTURAL ORDERING OF COAL CHAR DURING HEAT TREATMENT AND ITS IMPACT ON REACTIVITY

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Introduction

Structure ordering of carbon during heat treatment has long been reported [1]-[3]. The orientation as well as the size of the crystallites inside the disordered carbon is altered by thermal energy. With increase of the severity of heat treatment, the disordered carbon tends to form a graphitic structure, which has a very ordered arrangement of crystallite layers with a large extension in both the a- and c- axes.

Coal char is inherently very disordered in structure. However it could become graphitized because of the high temperature at which it is gasified or combusted. Experimental results have shown that the reactivity of coal char could decrease many orders of magnitude after heat treatment for only a few seconds [4-6]. This so-called thermal deactivation has been related to the structure ordering [7], but with few supporting experimental data. The present paper studies the structure of a heat treated Australian coal char using XRD, HRTEM and electrical resistivity techniques and relates it with its subsequent reactivity in oxygen.

Experimental

An Australian semi-anthracite, Yarrabee, was sieved to within a particle size range of 90-106 μm and then washed in HCl and HF acids to remove the mineral matters. The raw coal and the ash-free coal were then heat treated in a tube furnace at various temperatures (850 – 1150 °C) for various times (2min – 15 hours).

The heat treated coal chars were subject to XRD, HRTEM, electrical resistivity and reactivity tests. The XRD patterns were analyzed for the structural parameters using two methods. One is the classical Scherrer's equation and the other is the structural refinement technique of Shi et al. [8]. The high resolution transmission electron microscope (HRTEM) images were obtained using a JEOL2010 transmission electron microscope (structure resolution limit 0.25 nm). The elemental composition of the samples were analyzed using an Oxford-Link silicon-crystal energy dispersive X-ray spectrometer which is attached to the 2010 electron microscope. The HRTEM images were captured onto Kodak SO-163 electron image film and digitised using a Leafscan 45 negative scanner.

Electrical resistance was measured over a fixed bed size for all the chars using an ohmmeter (Hioki 3220 m HiTester, range 20m to 20K, accuracy 0.2 %). Details can be found elsewhere [9]. Reactivity was tested using a thermogravimetric analyzer (Cahn TG-121). The reaction temperature was fixed to be 673 K and pure oxygen was used as oxidizer. The reaction rate reported is defined as the reaction rate per gram of combustible carbon at 1 % conversion.

Results and Discussion

The structural parameters of the coal char after heat treatment, obtained by fitting the XRD patterns using the Shi et al. model [8], are shown in Figure 1. The crystallite size increases only slightly with the increase of heat treatment temperature and time, indicating that crystallite growth is not important in the temperature range studied. The results obtained by using Scherrer's equation are similar to the above results, although the absolute values of L_a and L_c are significantly lower. The internal surface area of the coal char, calculated using the structural model of Bhatia [10], showed that the surface area based on the crystallite size by Scherrer's equation is much higher than the measured value, while that based on the values of L_a and L_c the Shi et al. model gives closer results. Therefore, Scherrer's equation appears to under-estimate the crystallite size.

The fraction of organized carbon, which is defined as the fraction of carbon having parallel layers in the crystallite, was obtained using the Shi et al. model. The variation of the fraction of organized carbon, g, with the heat treatment time and temperature is shown in Figure 2. It is clear that for the raw coal char the g value increases with increase of temperature and time, seemingly approaching an equilibrium value at each temperature. However the g value for the ash-free coal char does not change with increase of heat treatment time. This suggests that the mineral matter in the raw coal char promotes structural ordering.

The variation of the electrical resistivity with the heat treatment time and temperature was also measured, supporting the above results. The electrical resistivity of the raw coal char decreases with increase of heat treatment time and temperature while that of the ash-free coal char does not change significantly. The coal chars were
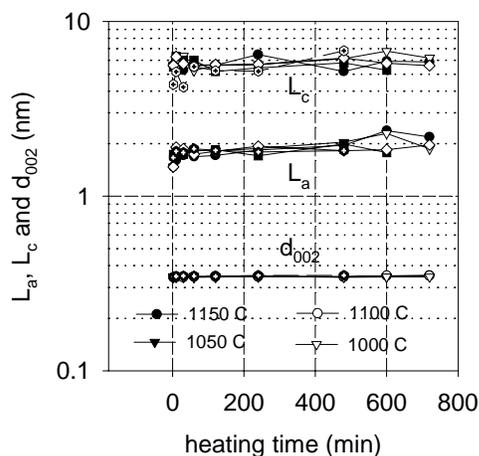
Figure 1. Structure parameters of the raw Yarrabee coal char and the ash-free coal char after heat treatment at various temperatures for various times, obtained using the Shi et al. structure refinement program. Hexagons represent data for the ash-free coal char heat treated at 1150 C for various times. d_{002} is the distance between two graphene layers.
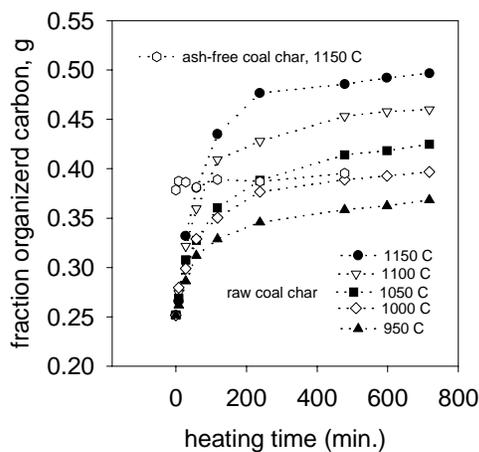

Figure 2. Fraction of organized carbon in the raw Yarrabee coal char, and in the ash-free coal char, after heat treatment at various temperatures for various times.

observed under a HRTEM and the images showed that the structure of the areas around the iron particles is very ordered while the structure in the areas away from the iron particles is still disordered. All these results indicate that structural ordering of the crystallite layers is important in the temperature range studied, and iron is acting as an effective catalyst.
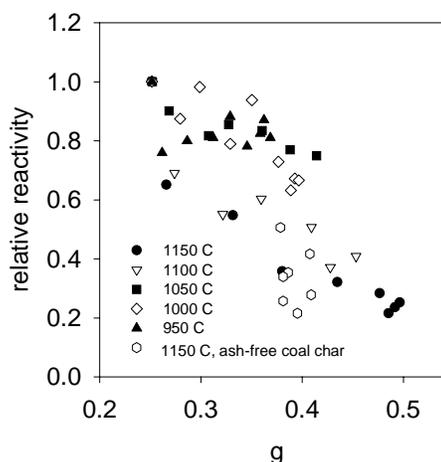

Figure 3. Correlation of the electrical resistivity with the fraction of organized carbon, g, for the raw coal char and the ash-free coal char, after heat treatment at various temperatures for various times.

A good correlation between the reactivity of carbon with the fraction of organized carbon is found in Figure 3, suggesting that the reactivity of carbon is influenced by the structural ordering.

A number of models including Pacault's [11] superposition method, various reaction models and a diffusion model were used to fit the data in Figure 2. The diffusion model gave the best results, suggesting that the structural ordering is controlled by a diffusion process. A low apparent activation energy of 11.8 kJ/mol was obtained for the diffusional ordering process. The approach to an equilibrium in Figure 2 suggests that the ordering occurs through a two step sequence with the first being a rapid diffusion controlled endothermic step that is nearly at equilibrium, and the second a slow irreversible exothermic step. The apparent heat of the first step is found to be about 71.7 kJ/mole.

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