STACKING STRUCTURE OF AROMATIC LAYERS IN DTF COAL CHARS AND ITS RELATION TO GASIFICATION PROPERTY

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Introduction

Gasification property or reactivity of coal char has often been discussed with the microstructure of a sample. Pore structure of a sample is important for the accessibility of reaction gas, which is often considered in simulation studies for the prediction of gasification reactions. Also, study of crystallographic structure in a solid part could lead to a lot of microscopic information of a char sample. Generally, solid part of coal char consists of aromatic carbon layers existing separately, or in parallel with each other to form graphitic stacking structure. There are also a considerable amount of carbon atoms out of aromatic layers depending upon heat-treatment conditions of a sample. X-ray diffraction (XRD) measurement is a powerful technique to study the structure of carbon materials with such characteristics. So far, many authors[1,2] used the results of XRD measurements in their studies, mainly for comparing the reaction rate to the crystallite sizes. A stacking height, on the other hand, has been almost not related to gasification properties of a char sample. But carbon crystallites composed of single or stacked aromatic layers are often considered to act as walls of "slit-shaped micropores". This slit-shaped model is now widely regarded as a reasonable model of micropores in carbon materials. Therefore, the stacking structure of aromatic layers estimated by an appropriate method can be related to the gasification reactivity of a char.

One of the difficulties, however, in using the structural parameters by a XRD measurement for a numerical characterization of coal char is a degree of accuracy. Size of graphitic crystallite is often estimated with Scherrer's equation in many cases. But this method is based on the assumption that the sample is composed of crystallites in the same size, which is far from the fact confirmed by the observations with transmission electron microscope (TEM). Instead, some of us have standardized the characterization method named STAC-XRD analysis, based on the earlier studies by Hirsch[3] and Shiraishi[4].

In this paper, we numerically characterized the stacking structure of aromatic layers in 10 types of coal chars by STAC-XRD method, and investigated the relationship of the structural parameters to a gasification property of the sample.

Experimental

XRD measurement. STAC-XRD method aims especially at characterizing the stacking structure of aromatic layers in carbonaceous substances or carbon materials with less crystallinity. The process is described in detail elsewhere[5,6]. Briefly, the parameters below are evaluated by this method: interlayer spacing (d_{002}), stacking index (*SI*; related to crystallinity), distribution of the number of stacking aromatic layers per stack (*N*), and the average number of layers per stack (N_{ave}). Among all these parameters, *N* distribution and N_{ave} are calculated by the statistic method assuming the distribution of crystallite size. XRD patterns were measured at 2 =10-41˚ by the step-scanning method (=0.2˚, 25 second at each angle) using a Rigaku RU-300 goniometer with CuK radiation under 40kV-80mA operating conditions. A peak corresponding to the carbon 002 reflection is included in this range.

Gasification property. The parameter T_{cr} was used to indicate the reaction property. This was originally established by Advanced Fuel Research Inc.[7] as a reactivity index at an early stage of gasification. The determination of T_{cr} relies on a thermogravimetric analysis technique, in which the weight loss is measured while the sample is heated at a constant rate in the presence of a reactive gas. For further details of the determination process of T_{cr}, see ref.7.

Samples. Original coals (60 mesh size under) listed in Table 1 were stirred in HCl (18 %) at 50 ˚C for 8 hours, followed by a drying process at 105 ˚C. According to the analysis of ash content, Ca and Fe were removed below 0.1 wt% by the deashing of all the samples. The deashed coals were then heat-treated in a N_2 flow in a drop tube furnace (DTF; 1150 mm in height, 42 mm in diameter) in which the temperature was controlled at 1723 K. The residence time was approximately 1.5 seconds. Original coals without the acid-treatment were also heat-treated for comparison. BET specific surface areas of the deashed chars also shown in Table 1 were determined by the measurement of CO_2 adsorption isotherms at 303 K.

Results and Discussion

STAC-XRD analysis clarified that, concerning *N* distributions of deashed chars, aromatic layers included in the stacks with *N*=2 and 3 accounted for 65-80 % of all stacking layers in all the char samples. Most of them indicated the gradual declines of fractions with the increase of *N*, while some chars made from coals with higher C contents, such as SS037 and SS035, obviously showed the development of stacking structure with larger *N*: fraction of *N*=3 had a higher proportion than *N*=2, and a ratio of *N*>4 occupied over 20 %.

Figure 1 and 2 indicate the N_{ave} and *SI* of every sample plotted against their T_{cr} values. It is very clear that these structural parameters of demineralized chars have stronger correlations with T_{cr} than non-demineralized ones. In other words, characteristics of the stacking structure described with the parameters N_{ave} and *SI* can be fundamentally linked with the concentration of active site for the gasification reaction. We cannot found good correlation like this between %C and T_{cr} for the same series of chars. Concerning the difference of chars originated from the same coal, the deashed chars moderately tend to have smaller N_{ave} and larger *SI* with smaller T_{cr} than the non-deashed chars. The trend is, however, not proportional to the amount of specific elements in ash. At least, the chars from coals including relatively more amount of Ca (wt% of total ash, as CaO; 7.4 % in SS037; 8.54 % in SS027; 9.55 % in SS005) have a large difference in their *SI* values between deashed and non-deashed status. The element Ca in ash has been considered as catalyst for coal gasification. By the TEM observation, we could not see any distinctive features even around the metal particles, but found some regions in which aromatic layers of 1-1.5 nm are oriented along the surface of the particles.

Table 1. List of original coals used in this study.

sample	Elemental analysis (wt%, daf)					Ash /wt%	Surface area of deashed char /m^2g^{-1}
	C	H	N	S	O		
SS037	90.64	4.23	1.30	0.40	3.44	16.54	20.6
SS035	88.31	5.14	1.58	0.48	4.49	14.54	26.6
SS021	84.38	4.67	1.95	0.46	8.54	14.43	29.2
SS008	82.37	5.40	1.78	0.44	9.64	11.90	24.0
SS002	81.20	6.06	1.57	0.58	10.59	14.52	28.5
SS027	80.61	4.93	1.01	0.68	12.77	10.24	29.7
SS005	78.72	6.22	1.17	0.11	13.78	12.08	29.4
SS034	78.30	6.75	1.32	0.74	12.89	8.69	37.8
SS026	76.82	5.78	1.39	0.34	15.67	12.48	28.7
SS039	74.72	5.58	1.59	0.27	17.85	12.00	68.1

More specifically for every structural parameter, T_{cr} increased with the increase of N_{ave}. Development of stacking structure in the direction of stacking height can cause a closure of slit-shaped micropores, considering that the micropores of this type is basically formed by a mis-configuration among layers or stacks. This view is also supported by the result of specific surface areas (Table 1). It is necessary, at this point, to explain the concentration of active sites for gasification reaction of coal char in connection with the total surface area (TSA). The concept of active sites is often expressed with active surface area (ASA)[1] determined by an oxygen chemisorption measurement. From the structural point of view, it is also related to the size of aromatic layers, as mentioned in the first section of this paper. We have not estimated ASA values for every deashed char sample in this study. But the TEM observation found out that there are very few differences in layer sizes (ca. 1nm) among these char samples. It means that we do not have to take too much into account the difference of reactivity due to the size of aromatic layers. ASA values of every deashed char can be therefore influenced by the accessibility of reactive gas, i.e., open pore structure as well as stacking structure of aromatic layers constituting the pore walls. Also in a simplified image, porous texture including stacks with fewer aromatic layers is more reactive because of these layers having more occasions of exposure to the reactive gas. The relationship between T_{cr} and N_{ave} is consistent for the reason above. The similar results were provided by the observation with TEM[2].

As for *SI*, it also increased with the increase of T_{cr}. Definition of *SI* represents the ratio of carbon atoms contributing to the stacking structure, and accordingly the subtraction 1-*SI* gives the relative amount of carbons present in single aromatic layers or on the periphery of aromatic layers. It is likely that around single layers the structure is ordered relatively locally, which would produce more microporous region than around the stacking structure. It is also well known that carbon atoms out of the crystalline component are preferentially oxidized in themselves due to their higher reactivity than those in the crystalline component. Interlayer spacings (d_{002}), on the other hand, did not show any clear correlations with the reaction parameters. It is presumably because that the carbon 002 peaks in all the samples were too broad to indicate the strict positions of maximum intensity.

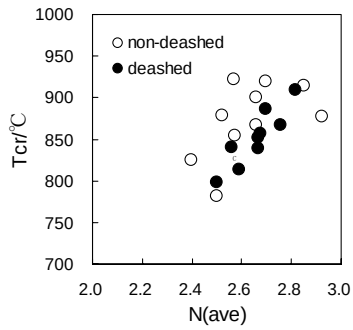

Figure 1. Reaction parameter T_{cr} plotted against the average number of aromatic layers in a stack (N_{ave}).

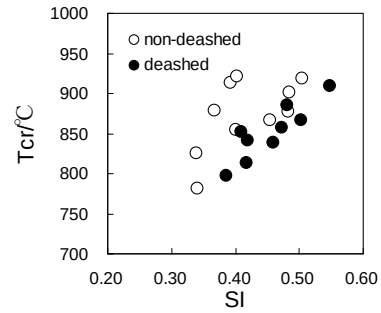

Figure 2. Reaction parameter T_{cr} plotted against the stacking index (SI).

Conclusions

We found that the structural parameters obtained by STAC-XRD were proportionally related to the gasification properties at an early stage of gasification process, which is consistently explained by the slit-shaped micropore model.

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