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A. Ziegler, K.H. van Heek,
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Laser raman microscope and XPS investigations on char reactivities

S. Kambara[a], Y. Fusegawa[a], T. Yamada[b], M. Harada[c] and S. Shinozaki[c]

a Idemitsu Kosan Co. Ltd., Coal Research Laboratories. 3-1 Sodegaura, Chiba 299-02, Japan
b Idemitsu Kosan Co. Ltd., Energy Development Department. No. 3-6 Kita-Aoyama 1-chome, Minato-ku, Tokyo 107, Japan
c Center for Coal Utilization, Japan. 6-2-31 Roppongi, Minato-ku, Tokyo 106, Japan

ABSTRACT

To examine effects of carbon structure on char reactivities, variation of carbon structure in residual carbon during combustion was investigated by laser raman microscope (LRM) and X-ray photoelectron spectroscopy (XPS) techniques. The char samples of 10-99% unburnt carbon were obtained from pulverized coal combustion test lig for two different coals. Raman spectra measurement for many residual carbon fragments gave information on the distribution of carbon structure change, XPS C1s spectra are available to track the state of C-O bond on the carbon surface. Specific parameters to evaluate essentially the char reactivities are studied based on both spectra analysis.

Keywords: gasification, combustion, reactivity, structure

1. INTRODUCTION

In Japan, most of the steaming coal has been imported from various coal producing countries such as Australia, United States, China, Indonesia, South Africa, Russia and Canada. Since it is required to use a wide variety of coals in a utility, evaluation of acceptability of potential imported coals, more than 100 different coals, is one of the most critical issues for coal users.

Char combustion and gasification rate are the most important controlling factors to determine the acceptability of coals in combustion or gasification efficiency. The char reactivities is controlled by chemical kinetics at low temperatures, oxygen pore diffusion at moderate temperatures and oxygen bulk diffusion at high temperatures. It is seems reasonable to suppose that chemical structure of residual carbon plays a pronounced role

in the char conversion because the final stage of reaction processes in the reactors is low temperature.
It is necessary to employ an available factor which represents accurately effects of carbon structure on char reactivities to predict carbon burn out in pulverized coal combustion, fluidized bed combustion, and carbon conversion in coal gasification for various coal types. The objective of the present paper is to examine carefully the variation of carbon structure in char during combustion, and to determine evaluation parameters from LRM and XPS spectra,

2. EXPERIMENTAL

2.1 Coal samples

Some basic information on the coals used in this study are listed in Table 1. Those coals are chosen to discriminate clearly the difference of carbon structure in both chars, it was found that coal SS001 is inferior to coal SS005 in char reactivity from combustion test results.

Table 1: Fuel analyses

Coals	VM %,db	FC %,db	Ash %,db	C %,daf	Vitrinite %	Exinite %	Inertinite %
SS001	28.6	56.3	15.1	84.1	46.0	9.3	44.7
SS005	46.6	41.2	12.2	78.4	89.6	8.3	2.1

2.2 Char samples

The laboratory-scale pulverized combustor [1] was employed to correct chars during combustion, and has a diameter of 30cm and is 2.5m long. The coal feed rate was controlled to 6 - 7kg/hr to keep 4.2% O_2 in the flue gas under staged combustion. Seventeen sampling ports, SP1 to SP17, were provided along furnace wall every 15 cm for analysis of gas composition, solid sampling and temperature measurement during combustion. The nine char samples were obtained with a water-cooled probe, which were investigated the variation of carbon structure by LRM and XPS techniques.

3. RESULTS

3.1 LASER LAMAN INVESTIGATIONS

Raman spectroscopy is potentially a very useful technique for characterizing heterogeneous carbons. The measured spectra were exited by the green line (514.5nm) of an argon ion laser with the low laser power (0.65mW at sample surface) and 2μm diameter in order to avoid sample-heating effect. The polished sample was placed under the microscope objective x50 which was attached XY stage, and more than 50 points of residual carbon were measured.
Figure 1 shows averaged spectra for 4 chars of coal SS001 which were corrected at different sampling point. As several previous works reported [2-4], the presence of

graphite band (G-band) at 1580 cm^{-1} and disordered band (D-band) at 1380 cm^{-1} are recognized. Both G-band and D-band intensity are decreased with increasing carbon conversion. Some quantitative parameters were defined to characterize carbon structure, example for ID/IG, ID/IV and IG/IV. Where, ID, IG and IV are intensity of D-band, G-band and V-band meaning valley of spectrum between D-band and G-band, respectively. From the results of comparison some parameters with carbon conversion, it is found that ID/IV and ID/IG are good relationship with variation of carbon conversion. ID/IV fully expresses the defference of carbon structure in high carbon conversion at final stage of combustion than ID/IG because of exponential function as shown in figure 2(a) and figure 2(b). ID/IV value of SS001 is lower than that of SS005 at any carbon conversion. Low ID/IV value might mean high reactivities of chars.

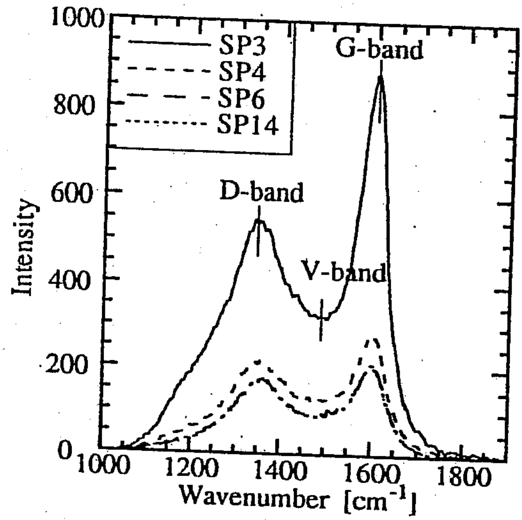

Figure 1: Raman spectra for 4 different chars from SS001 during combustion.

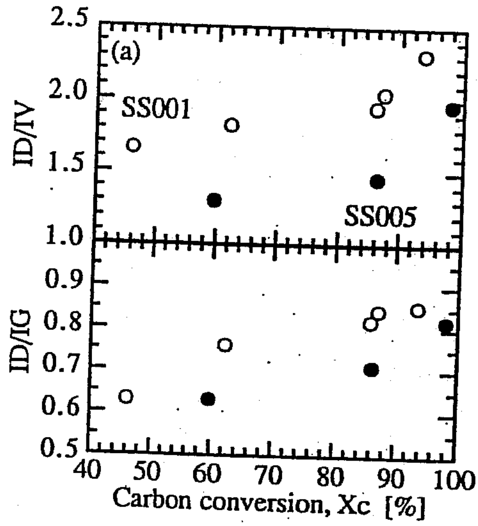

Figure 2: Variation of two parameters calcurated from raman spectra during combustion.

3.2 XPS INVESTIGATIONS

The X-ray photoelectron spectroscopy technique was used to determine the bonded state of oxygen combined with carbon on the char surface. The char sample was mounted uniformly by pressing onto a special stage of 20 mm diameter with a double-sided adhesive tape, which was measured with an X-ray source power of 300 watts at a pressure of below $1x10^{-6}$Pa. The measurement was carried out three times at the different surface positions to obtain averaged quantitative data.

Figure 3 shows carbon (1s) spectrum for SS001SP4 char including a curve resolution at 285.0, 286.3, 287.5, and 289.0eV [5]. Variation of total oxygen including three kind of the oxygen functional forms, ether, carbonyl, and carboxylic groups, are examined as a function of carbon conversion as shown in Figure 4. The fraction of the total oxygen of SS001 is elevated strongly with progress in combustion. It is likely that the desorption of oxygen from the carbon surface for SS001 having low reactivity chars is slower than that of SS005. The desorption rate of oxygen obtained from Figure 4 may be able to use as an evaluation factor of char reactivities as well as ID/IV value from raman spectrum.

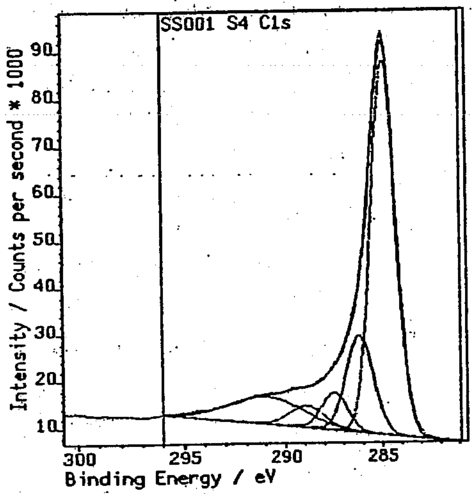

Figure 3: XPS C1s spectra for SS001SP4 char including a curve resolution

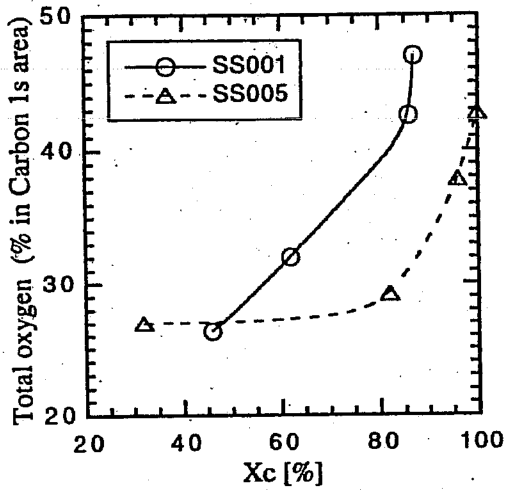

Figure 4: Variation of total oxygen as a function of carbon conversion.

4. CONCLUSIONS

Laser raman microscope and X-ray photoelectron spectra are obtained for various carbon conversion of chars to determine an available factors to evaluate accurately char reactivities under chemical reaction control. ID/IV value calculated from raman spectrum and the fraction of total oxygen obtained from XPS C1s spectrum reflected the behavior of char reactions. It is likely that char reactivities is high when it has low ID/IV value and high desorption rate of oxygen.

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