

THE USE OF STEP SCAN FT-IR/PAS FOR THE STUDY OF STRUCTURAL CHANGES IN COAL AND CHAR PARTICLES DURING GASIFICATION

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INTRODUCTION

To understand the reactions occur during coal gasification, it is essential to investigate reactivity and structural changes in coal and char. As coal and char are solid which hardly dissolve into most of solvents, variety of applicable methods for analyses is limited. An FT-IR spectroscopy is a promising method to detect the status of various kinds of functional groups and their chemical and physical changes. Recently, FT-IR photoacoustic spectroscopy(FT-IR/PAS) of coal has been intensively studied.¹ Depth profiling analyses using FT-IR/PAS is also discussed focusing on the technique to avoid a saturation of the photoacoustic signal.²⁻⁴ In this paper, a step scan FT-IR/PAS with a phase modulation was applied to depth profiling of coal particles whose surfaces were treated by oxidation and ion-irradiation to elucidate a sampling depth. Depth profile of gasification char particles obtained from HYCOL entrained flow type gasifier were analyzed by step scan FT-IR/PAS.

EXPERIMENTAL

Preparation of oxidized coal samples

20g of Miike coal(C: 82.2%, daf; H: 6.2%, daf; N: 1.0%, daf; ash: 7.7%, dry, 24-60mesh) was placed in a glass-made, constant volume closed reactor equipped with a circulator, and was dried at 150°C under vacuum for 3 weeks. Oxidation reaction was initiated by introducing oxygen from the reservoir to the reactor maintained at 100°C. Pressure drop was monitored by pressure gauge(Balzers APG010) to calculate the amount of oxygen absorbed into coal.

Taiheiyo coal(C: 74.6%, daf; H: 6.6%, daf; N: 1.4%, daf; ash: 12.9%, dry; particles of 2-5mm) was held in a stainless steel wire mesh and oxidized in a air stream heated up to 300°C for 1h.

Oxidized coal samples were used for FT-IR/PAS analyses without further pulverization. After IR analyses, each sample is mixed with phenol resin, solidified and polished to make a cross sectional observation by a microscope using reflected light with an oil immersion method.

Preparation of ion-irradiated coal

Taiheiyo coal(60-100mesh) was dried under vacuum($\sim 10^{-4}$ torr) at 170°C for 3 weeks. 4g of the dried coal was exposed to irradiation of argon ion with energy of 100keV for 4h using 200keV ion implanter(B) at Ion Engineering Center Corporation(Osaka, Japan).

Gasification Char

Chars were produced from Taiheiyo coal and Muswellbrook coal(C:80.3, daf, H:5.5, daf, N:1.7, daf, ash 11.7%, dry) during the operation of HYCOL gasifier (Chiba, Japan)⁵.

FT-IR measurement

A Biorad FTS-60A/896 step scan FT-IR spectrometer was used for all spectral measurements. Spectra were recorded at resolution of 8cm⁻¹ using an MTEC model 100 photoacoustic cell with its accompanying preamplifier/power supply. Helium was used as the carrier gas in the PA cell. Stanford Research Systems SR510 lock-in amplifier was used when phase modulation was applied. Step scan speed/phase modulation frequency of 10/100Hz and 50/400Hz was used for the FT-IR measurement.

RESULTS AND DISCUSSION

Step scan FT-IR/PAS with a phase modulation

FT-IR/PAS has been in use for about ten years.² Many photoacoustic applications involve the study of the spectra for layered and heterogeneous samples with varying interferometer scanning velocity, to probe deeper into them

as the velocity is reduced. The main advantage of step scan interferometry for PAS is that a single modulation frequency can be applied over the entire spectral range to generate the PA signal. Step scan data collection for depth profiling experiments produces a constant sampling depth across the spectrum for each frequency used.⁴ Spectrum obtained without phase modulation is quite photoacoustically saturated, but the phase modulated spectra are not. Among the vector component of PA signals, in-phase(0°) component carries response of deep layer and quadrature(90°) component takes signal of surface layer. In principle, by changing the phase angle of the lock-in amplifier, it should be possible to probe different depths of the sample with the same depth for all infrared frequencies in the spectrum.

Oxidized coal

Results of oxidation of Miike coal is summarized in Table 1. Main product in gaseous phase was water. Approximately one half of total amount of oxygen reacted(O_{react}) was consumed to form H_2O , CO and CO_2 . Oxidized coal samples which gained 0.54~2.36%(initial coal weight basis) of oxygen was consequently obtained. Photoacoustic spectra recorded at 2.5kHz(rapid scan) were shown in Figure 4. PA spectrum of unoxidized(dried) Miike coal recorded at the same FT-IR settings was used for reference.

Absorption peak at around $1700cm^{-1}$, attributable to carbonyl group, increased by oxidation. Broad peak reflects various kinds of carbonyl entities. Shoulder peak observed at higher than $1700cm^{-1}$ is attributed to ester or carboxylic acid. Small peaks detected at $1540cm^{-1}$ may be attributed to carboxylic ion. Besides, peaks at $2800\text{--}3050cm^{-1}$ decreased with oxidation indicating that reaction of dehydrogenation from mainly aliphatic compounds proceeded. Absorption increased around $3400cm^{-1}$ can be attributed to formation of hydroxyl group. PA spectra obtained here seems to be quite similar to those acquired by diffuse reflectance FT-IR spectroscopy⁶ except OH region.

Depth profiling analyses of a series of oxidized coal samples was performed by using step scan mode(step speed/phase modulation frequency = 50Hz/400Hz). Figure 2 illustrate step scan FT-IR/PA spectra of oxidized Miike coal which are measured and phase-separated with phase angles of 45° and 0° respectively. PA spectrum of unoxidized Miike coal was used for background correction. In the layer near surface detected with phase angle of 45° (A), absorption at $1700cm^{-1}$ and $1100cm^{-1}$ increased indicating the formation of oxygen containing functional groups such as C=O and C-O with increase in the amount of oxygen reacted with coal. On the other hand, peaks at $2800\text{--}3050cm^{-1}$ did not show a definite increase nor decrease with series of oxidation conditions. Similar tendency of the intensity changes in peaks was observed when phase angle was decreased to 0° to obtain the signals from deeper layer as shown in Figure 2(B).

It is assumed that oxygen containing functional groups formed by oxidation uniformly distributes in oxidized layer, but dehydrogenation reaction takes place mainly in the surface layer. Other interpretation may be that aliphatic compounds decomposed and released by oxidation moves inside coal particle with certain mobility.

Michaelian utilize an FT-IR spectrometer with STop-and-Go mode for depth profiling of oxidized coal and estimated the thickness of oxidized layer at $\sim 12\mu m$ corresponding to the modulation frequency of 200Hz.³ This estimation, however, involves some assumption. Measurement of actual sampling depth is required. Oxidized Miike coal samples were used for cross-sectional observation by microscope with reflected lights. No obvious oxidation layer could be seen by microscope observation, possibly due to the mild oxidation conditions. Taiheiyo coal oxidized at $300^\circ C$ was used for estimation of sampling depth of step scan FT-IR/PAS measurement. Figure 3 shows depth profiling PA spectra of oxidized Taiheiyo coal with various modulation frequencies and phase angles. PA spectra of unoxidized Taiheiyo coal was used for back ground correction to compare the changes in peaks before and after oxidation. When modulation frequency of 400Hz and phase angle of 90° were selected, the vicinity of coal surface should be detected. Considerable decrease in peaks at $2800\text{--}3050cm^{-1}$ attributed to CH stretching band was observed. Decreasing phase angle from 90° to 0° to obtain the signals of deeper layer, a peak at around $1700cm^{-1}$ attributed to C=O band increased. When modulation frequency is switched to 100Hz, infrared beam is expected to penetrate into deeper layer of coal particle. Applying the phase angle

of 90-45°, decrease in CH peaks was observed, while difference between PAS spectra of oxidized and unoxidized samples scarcely be detected with a phase angle of 0°. This indicates that changes in functional groups caused by oxidation occur only in the vicinity of coal surface.

Oxidized Taiheiyo coal samples were used for cross-sectional observation by microscope with reflective lights. 5-10µm of bright rim was observed on the edge of coal particles. Unoxidized coal did not show this kind of rim. Thus, actual sampling depth of the spectrometer is estimated to around 10µm.

Ion-irradiated coal

Step scan FT-IR/PA spectra of ion irradiated coal measured with various modulation frequencies and phase angles are shown in Figure 4. PA spectra of untreated Taiheiyo coal obtained at the same FT-IR settings are used as background. In the spectra recorded with 400Hz of modulation frequency, peaks at 2800-3050cm⁻¹ and 1700cm⁻¹ obviously decreased indicating dehydrogenation and decarbonylation occurred during ion irradiation. On the other hand, changes in functional groups is scarcely detected when modulation frequency is set to 100Hz with a phase angle of 45° and below. According to the results of ion irradiation on metal surface, layer with a thickness of 1µm should be treated. Effects of ion irradiation on coal may be different and penetration depth is expected to deeper than 1µm in the case of coal. The spectra of ion treated coal seems to be consistent with the estimation from the oxidation experiment and microscopic observation of Taiheiyo coal.

Gasification char

A Taiheiyo coal char and a Muswellbrook coal char produced by HYCOL entrained flow gasifier are used for the IR measurement. No obvious absorbance peaks could be detected on the surface by the conventional FT-IR spectroscopy. In Figure 5, depth profiling FT-IR/PA spectra are shown. For better baseline correction, spectra of the char collected at the same time in different two places (cyclones CY-301 and 302) during the operation of HYCOL gasifier are mutually compared. Using step scan speed as slow as 10Hz to allow IR beam to penetrate deeply inside char, peaks at 2900cm⁻¹, attributed to CH, and broad peaks centered at 1700 and 3400cm⁻¹ could be clearly detected. These peaks directly indicate that some organic part including oxygen containing functional groups still remain inside the char particle after being processed at high temperature up to 1600°C. Two kinds of chars showed different depth profile. It is reported that almost all Taiheiyo char is categorized as network or Lacy type and Muswellbrook chars are mainly thick and thin walled balloon type⁵. Depth profile may reflect the difference of morphology of respective chars.

CONCLUSIONS

Step scan FT-IR/photoacoustic spectroscopy (PAS) was used for depth profiling of coal and gasification char particles. Phase modulation on the interferometer and phase separation at the detector, by a lock-in amplifier, and a variety of modulation frequencies and phase angles were used. The results showed considerably different spectra with depth of the coal. Sampling depth was estimated to ca 10µm by comparing the depth profiling spectra and cross-sectional microscopic observation of oxidized coal. Depth profiling of char obtained from HYCOL gasifier indicated the existence of an organic structure inside char particle. Considering that no obvious absorbance peaks could be detected by the conventional FT-IR spectroscopy, the use of step scan FT-IR/PAS is concluded to be a promising method for the analyses of even high temperature gasification chars as well as coals.

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Table 1 Results of oxidation of Miike coal ^a

Run	Time / h	O ₂ react ^b / mmol	Gaseous products / mmol					Analyses of oxidized coal		
			H ₂ O	CO	CO ₂	CH ₄	C ₂ +	O ₂ abs ^c /wt%	C% ^d	H% ^d
1	26	5.62	3.42	0.16	0.46	- 0	- 0	0.54	81.5	6.20
2	51	10.54	4.55	0.35	1.11	- 0	- 0	1.07	81.2	6.17
3	124	17.69	10.23	0.63	1.66	0.01	- 0	1.79	80.6	6.08
4	384	25.17	15.14	0.99	2.63	0.01	- 0	2.36	79.9	6.02

a) 20g of coal was used. Reaction temp: 100°C b) The amount of oxygen reacted with 20g of coal.
c) The amount of oxygen absorbed in coal. d) Ultimate analysis data, daf basis.

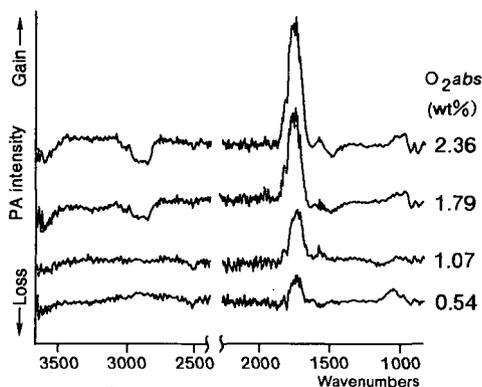


Figure 1 Photoacoustic spectra of oxidized Miike coal recorded at 2.5kHz (rapid scan mode). Spectrum of unoxidized Miike coal is used as background.

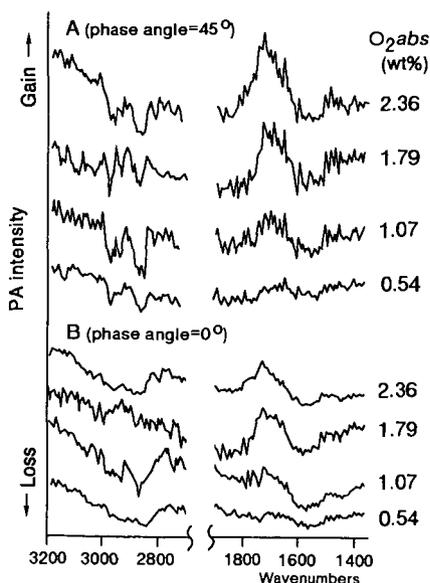


Figure 2 Step scan FT-IR/PA spectra of oxidized Miike coal measured with step scan/phase modulation freq. = 50/400Hz. Spectrum of unoxidized Miike coal is used as background.

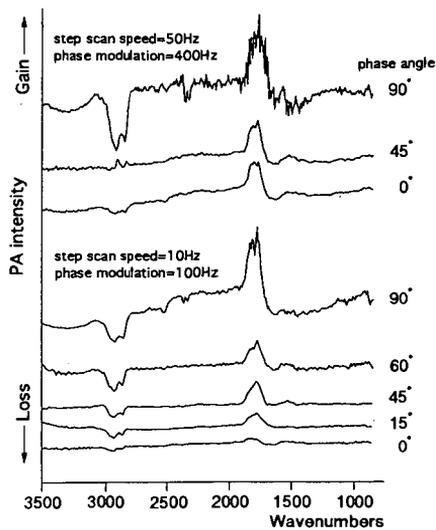


Figure 3 Depth profiling FT-IR/PA spectra of oxidized Taiheiyo coal. Spectrum of unoxidized Taiheiyo coal is used as background.

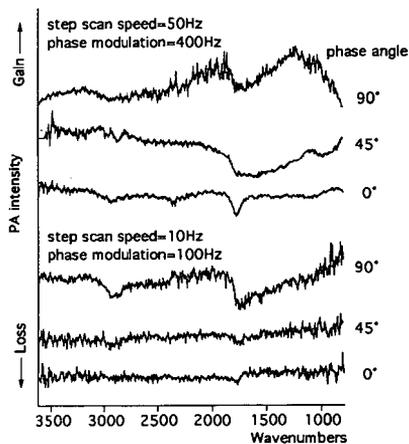


Figure 4 Depth profiling FT-IR/PA spectra of ion-irradiated Taiheiyo coal. Spectrum of untreated coal is used as background.

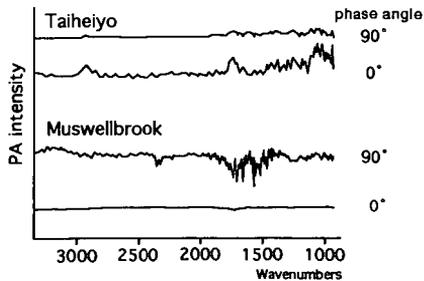


Figure 5 Depth profiling FT-IR/PA spectra of gasification chars obtained from HYCOL gasifier measured with step scan/phase modulation freq. = 10/100Hz.