XANES analysis of sulfur form change during pyrolysis of coals

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Three kinds of coal and their density separated samples were rapidly pyrolyzed in a free-fall reactor under a nitrogen stream at a terminal temperature of 1253 K. X-ray absorption near edge structure analysis was applied to directly determine the sulfur forms in the coal and pyrolysis char. The results showed that the low-density group contained sulfide and sulfoxide, which could contribute to the high extent of organic sulfur removal. Thermally stable thiophenic sulfur was observed in the higher density groups as a major form of organic sulfur.

Keywords: XANES, coal, sulfur form, pyrolysis

1. Introduction

Sulfur in fossil fuel resources, which causes several issues that impede their utilization, is the main element of air pollution, acid rain and corrosion in process plants. In the development of advanced electric power generation processes with combined cycles, the efficient desulfurization of coal is one of the most important and key technologies for the overall process design.

Th development of a coal cleaning process requires an accurate understanding of the organic sulfur forms in coal. ASTM (D2492) based on acid extraction is generally used for determining sulfur forms (pyritic, ferrous sulfide, sulfate and organic sulfur), though organic sulfur species cannot be distinguished. Temperature-programmed decomposition and temperature-programmed oxidation methods were tried to analyze the various sulfur forms in coal (LaCount et al., 1987). Sharp peaks of hydrogen sulfide and sulfide dioxide cannot be easily obtained though these are necessary to speculate on the sulfur forms. While solvent extraction has also been tried to analyze the different sulfur forms in coal, the limited extractable amounts of the organic sulfur induced and thermally changes makes the interpretation of observed results difficult (Buchanan et al., 1988). Recently, X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) have been used successfully to elucidate organic sulfur forms in coal and heavy hydrocarbons (Kelemen et al., 1990; Huffman et al., 1991).

In the present study, the organic sulfur forms were determined using XANES for high sulfur lignite, subbituminous and bituminous coals. Rapid pyrolysis was carried out to observe the desulfurization behavior in order to investigate the organic sulfur distribution and their characteristic release behavior during rapid pyrolysis.

2. Experimental

Table 1 shows the proximate, ultimate, and sulfur-form analyses of the sample coals: Mequinenza (Spain), Muswellbrook (Australia) and Illinois No.6 (USA). The samples were crushed, sieved, and then dried at 380 K. The average particle size of the samples was 0.35 mm. The samples were then separated into three groups by a sink-float method using different concentrations of a zinc chloride aqueous solution and a separating funnel. The absence of zinc chloride in the density-separated samples was confirmed by extraction with 5 M HCl for 2 h (Sugawara et al., 1994).

Rapid pyrolysies were performed using a free-fall pyrolyzer. This apparatus permits coal particles to be heated at rates from 10^3 to 10^4 K/s depending on the particle density and diameter. The longitudinal temperature profile along the reactor was controlled by an electric furnace composed of five sections, each of which was independently controlled. Temperature increases at a coal hopper exit and attains the highest value of 1253 K in the isothermal zone. The details of the apparatus have been described previously (Sugawara et al., 1991).

Some improvements to the ASTM (D2492) method and the Gladfelter and Dickerhoof method (1976) were used to analyze the sulfur forms (pyritic, ferrous sulfide, sulfate, and organic sulfur) in the raw coal and char. The details of the analytical method have been previously reported (Sugawara et al. 1988). Sulfur K-edge X-ray absorption near edge structure measurements were carried out at the beam line 2A of Photon Factory in the High Energy Accelerator Research Organization. Si (111) monochromators were used to select and vary the incident X-ray energy. The samples were attached to a nickel plate and placed in a vacuum chamber at 10^{-8} atm. Data were recorded in the fluorescence mode in the region of the sulfur K-edge at room temperature. The fluorescence spectra were collected using a scintillation counter. The absolute photon energy was calibrated to the peak absorption of K_2SO_4 at 2481.7 eV. Sulfur forms in the samples were determined by comparing the XANES spectra obtained to those for model compounds (Sugawara et al. 1999).

3. Results and Discussion

Figure 1 shows the third differential curves of the XANES spectra for the Mequinenza raw coal and char. A strong peak is observed in the range from 2471 to 2473 eV for the raw coal, which is attributable to sulfide, disulfide and thiophene. An intensive peak at 2474.5 eV results from sulfoxide (Sugawara et al. 1999). The third differential curve of the XANES spectra of the rapid pyrolysis char indicates that the sulfide and sulfoxide peaks become smaller after pyrolysis. The major component of organic sulfur in char is thiophenic sulfur.

Figure 2 presents the third differential curves of the XANES spectra for the Illinois No.6 raw coal and char. The curve of raw coal indicates the presence of sulfide, thiophene, and pyritic sulfur. The peaks of sulfide disappear after the pyrolysis. The above results are consistent with the pyrolysis of the model compounds. Aliphatic mercaptan and sulfide easily decompose below 1120 K, while thiophene and dibenzothiophene are resistant even at the high temperature of 1233 K (Calkins, 1987).

Figure 3 compares the extent of organic sulfur removal and carbon content for Mequinenza, Muswellbrook, and Illinois No.6 coals studied in the present work with that for previously reported 23

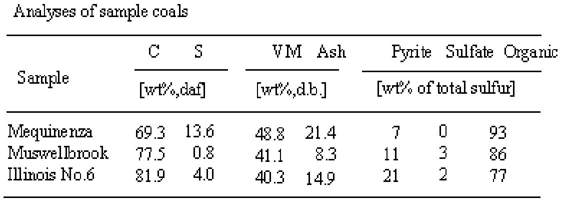

Table 1
Analyses of sample coals

Sample	C	S	VM	Ash	Pyrite	Sulfate	Organic
	[wt%,daf]		[wt%,d.b.]		[wt% of total sulfur]		
Mequinenza	69.3	13.6	48.8	21.4	7	0	93
Muswellbrook	77.5	0.8	41.1	8.3	11	3	86
Illinois No.6	81.9	4.0	40.3	14.9	21	2	77

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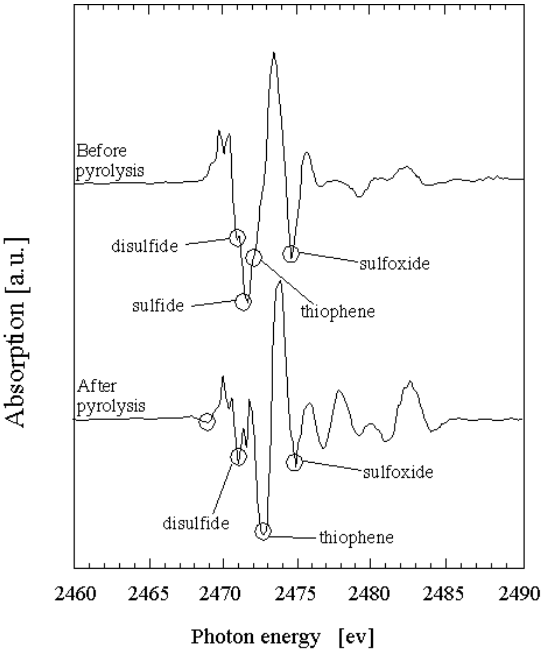

Figure 1
Sulfur XANES spectra for coal and char of Mequinenza.

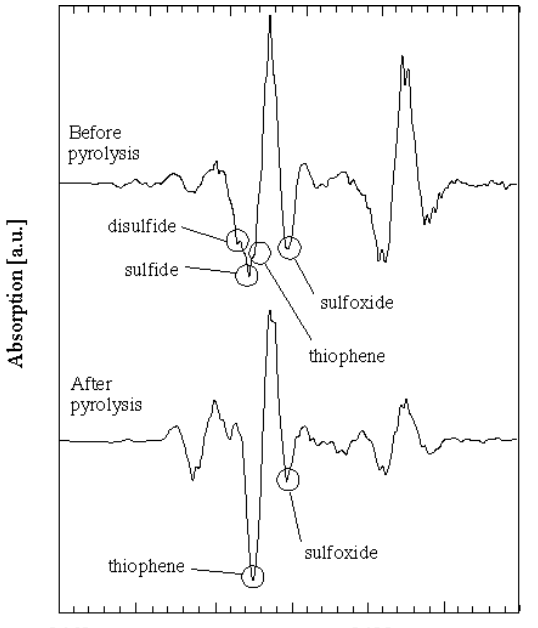

Figure 2
Sulfur XANES spectra for coal and char of Illinois No.6.

other coals. The carbon content ranges from 65 to 90% daf (Sugawara et al., 1997). The extent of organic sulfur removal is defined as {1 – (organic sulfur in char)/(organic sulfur in raw coal)} x 100 [%] where the ultimate content of organic sulfur in the rapid pyrolysis char (coal basis) was used as the organic sulfur in char. In Figure 3, an apparent linear correlation, however, cannot be obtained between the extent of organic sulfur removal during rapid pyrolysis and the carbon content of the raw coals. The samples containing around 75 % and 90 % carbon show the wide variation in the extent of organic sulfur removal.

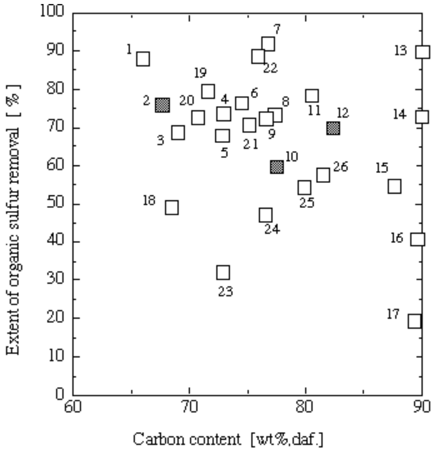

Figure 3
Change in extent of organic sulfur removal from solid phase with carbon content.

1. Fuxin
2. Mequinenza
3. Sheerness
4. Obed Mountain
5. Rosebud
6. Fushun
7. PSOC-830
8. PSOC-592
9. Yanzhou(x)
10. Muswellbrook
11. Ermelo
12. Illinois No.6
13. Furong
14. Yanzhou(B)
15. Smoky River
16. Nantong
17. Zhongliangshan
18. SS012
19. SS009
20. SS002
21. SS010
22. SS004
23. SS017
24. SS006
25. SS007
26. SS008

Huffman et al. (1989) reported that the content of sulfide sulfur decreased with the increase in the carbon content. George et al. (1991) found a linear increase in the percent of thiophenic sulfur to total organic sulfur from 45 to 95 % with an increase in carbon content. Because of the thermal stability of these organic forms, it is plausible that the extent of organic sulfur removal linearly decreases with the increase of carbon content due to the increase in the thiophenic sulfur content. In such a case, the extent of organic sulfur removal in rapid pyrolysis would decrease linearly with the increase of the carbon content of parent coal. The experimental results (Fig.3), however, do not show a linear relationship.

To investigate the possible effect of the local concentrations of a certain form of organic sulfur on the desulfurization behavior, the sulfur forms of density-separated coal samples were analyzed by XANES. Muswellbrook coal was separated into three groups, I (<1.26 g/cm^3), II (1.26 – 1.40 g/cm^3), and III (>1.40 g/cm^3) by a sink-float method. Figure 4 shows the third differential curves of the the XANES spectra for group I of Muswellbrook coal. The density-separated samples were pyrolyzed in a nitrogen stream using the free fall reactor. The XANES spectra of the char are also shown in Figure 4. Intense peaks of disulfide, sulfide, sulfoxide and thiophene were observed for group I. The curve of char for group I indicate the peak of thiophenic sulfur remained.

The third differential curves derived from the XANES spectra for group III are shown in Figure 5. Strong peaks of thiophene, sulfoxide and pyritic sulfur are observed for group III, while the sulfide peak was not detected. However, the pyrolysis char of

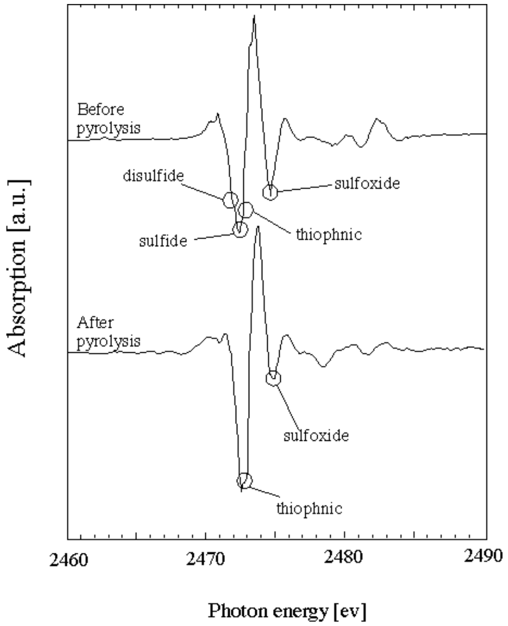

Figure 4
Sulfur XANES spectra for density separated group I of Muswellbrook.

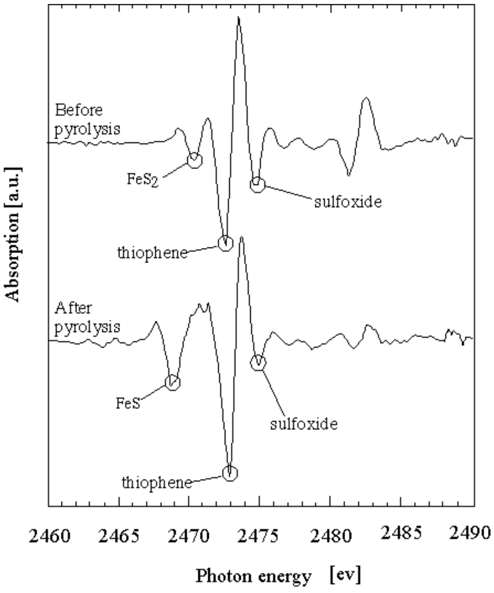

Figure 5
Sulfur XANES spectra for density separated group III of Muswellbrook.

group III clearly shows the peaks of thiophenic sulfur and ferrous sulfide; the latter was produced by the reduction of pyrite. The extent of organic sulfur removal during the rapid pyrolysis are 78% and 4% for groups I and III of Muswellbrook coal, respectively. It could be estimated that efficient desulfurization in a lower density group such as group I is related to the presence of thermally decomposable sulfide and disulfide.

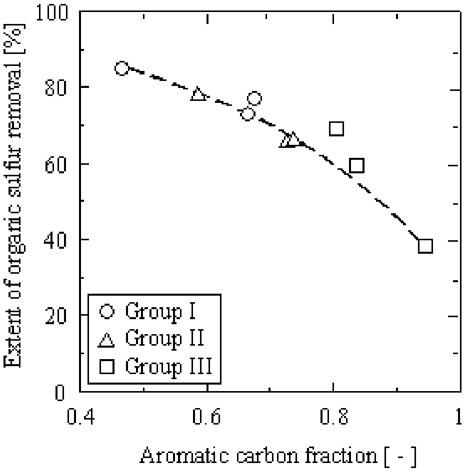

Figure 6
Relation between extent of organic sulfur removal and aromatic carbon fraction of density-separated coals for three kinds of coal.

The dependency of the extent of organic sulfur removal was correlated with the aromatic carbon fraction f_a of the density separated coals, where f_a was calculated using the following equation.

$f_a = \{1200 \times (100 - \text{Volatile matter})\} / (1240 \times \text{Carbon } \%)$

The correlation between the extent of organic sulfur removal in the density-separated sample and aromatic carbon fraction is shown in Figure 6. A fairly good correlation is observed between these parameters. The extents of organic sulfur removal smoothly decrease with the increase in the aromatic carbon fraction.

References

Buchanan, D. H., Osborne, K. R. Warfel, L. C. Wanping, M. Lucas, D. (1988). *Energy Fuels* **2**, 163-170

Calkins, W. H. (1987). *Energy Fuels* **1**, 59-64

George, G. N., Gorbaty, M. L. Kelemen, S. R. Sansone, M. (1991). *Energy Fuels* **5**, 93-97

Gladfelter, W. L., Dickerhoof, D. W., (1976). *Fuel* **55**, 355-359

Huffman, G. P. Huggins, F. E., Mitra, S., Shah, N., Pugmire, R. J., Davis, B., Lytle, F. W., Greegon, R. B., (1989). *Energy Fuels* **3**, 200-205

Huffman, G. P., Mitra, S., Huggins, F. E., Shah, N., Vaidya, S., Lu, F. (1991). *Energy Fuels* **5**, 574-581

Kelemen, S. R., George, G. N. Gorbaty, M. L., (1990). *Fuel* **69**, 939-944

LaCount, R. B., Anderson, R. R. Friedman, S. Blaustein, B. D. (1987). *Fuel* **66,** 909-913

Sugawara, T., Sugawara, K. Ohashi H. (1988). *Fuel* **67** 1263-1268

Sugawara, T., Sugawara, K. Nishiyama, Y. Sholes, M. A. (1991). *Fuel* **70**, 1091-1097

Sugawara, K., Tozuka, Y., Kamoshita, T., Sugawara, T., Sholes, M.A. (1994). *Fuel* **73**, 1224-1228

Sugawara, K., Gun-ji, T., Sugawara, T., Shirai, M., Nishiyama, Y., (1997). *Energy Fuels* **11**, 1272-1277

Sugawara, K., Sugawara, T., Shirai, M., (1999). *Jpn. J. Appl. Phys.* **38**, 608-611

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