

SULFUR BEHAVIOR IN VARIOUS CHEMICAL TREATMENTS OF COAL

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INTRODUCTION

Coal is abundant and low-cost energy resource and deserves increasing use in developing countries. Efficient precleaning technology must be developed for the utilization of high-sulfur and low-grade coals. Sulfur is a key component not only for the environmental conservation but also for the development of new coal utilization processes. Incomplete understanding of the behavior of organic sulfur during heat treatment has given rise to a misbelief that organic sulfur in coal cannot be removed by the pretreatments.

Development of surface analyses enables us to know the actual forms of organic sulfur in coal. XANES and XPS have been demonstrated as strong tools to elucidate organic sulfur forms in coal and heavy hydrocarbons.¹⁻⁴

We have demonstrated the dynamic behavior of sulfur forms during pyrolysis in a series of studies on chemical coal cleaning processes.⁵⁻⁷ These studies showed that rapid pyrolysis removed organic sulfur effectively in some types of coal. The release rate as well as the extent of organic sulfur removal increased with the contents of exinite and vitrinite. Part of the organic sulfur exist in a thermally stable form which is difficult to remove from coal by pyrolysis. Thermally stable organic sulfur remaining in the solid should be changed to decomposable forms to achieve efficient desulfurization in the pretreatment process.

In the present study, behavior of sulfur forms has been followed for lignite, subbituminous and bituminous coals in rapid pyrolysis. Chemical pretreatments were carried out to transfer the thermally stable form of reactive species before pyrolysis. Organic sulfur forms were determined by using XANES for coal before and after rapid pyrolysis with chemical pretreatments. Sulfur capture experiment was also conducted for rapid pyrolysis char in a nitrogen stream containing hydrogen sulfide to seek a new application to porous carbon.

EXPERIMENTAL

Table 1 shows proximate, ultimate and sulfur-form analyses for the sample coals, Spanish lignite Mequinenza, Australian subbituminous Muswellbrook, Chinese bituminous Nantong, and Montana subbituminous Rosebud coals. Average particle size of the sample was 0.35 mm.

Two kinds of chemical pretreatments were carried out as follows. The coal samples were immersed in a saturated aqueous solution of potassium hydroxide for 24 h with agitation at room temperature. The wet alkali immersed samples were then heated at 523 K for 4 h in a nitrogen atmosphere after filtration from potassium hydroxide solution. The alkali-treated samples were washed repeatedly with distilled water to reduce the basicity and then dried out at 380 K.⁸

Table 1 Analyses of sample coals

Sample	Ultimate [wt%, daf]					Proximate [wt%, db]		Sulfur form [wt% of total sulfur]		
	C	H	N	S	Diff.	VM	Ash	Pyritic	Sulfate	Organic
Mequinenza	69.3	5.5	1.0	13.6	10.6	48.8	21.4	7	0	93
Muswellbrook	77.5	6.0	2.1	0.8	13.6	41.1	8.3	11	3	86
Nantong	88.9	4.9	0.6	5.0	0.6	17.0	17.3	34	1	65
Rosebud	73.0	4.5	0.9	0.9	20.7	39.8	10.2	32	3	65

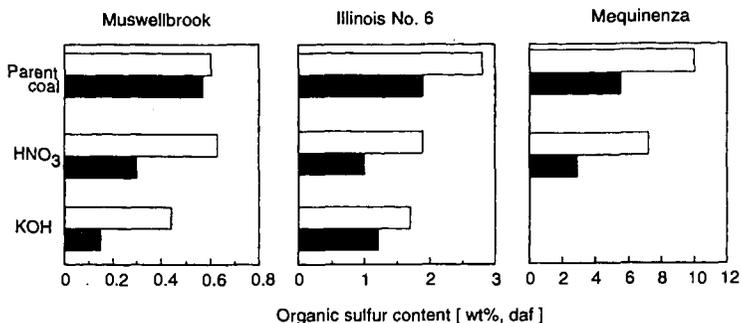


Fig.1 Change in organic sulfur content with various pretreatments (□, before pyrolysis; ■, after pyrolysis)

Nitric acid pretreatment was also carried out. The sample coals were immersed in nitric acid aqueous solution at a boiling temperature. After filtration and drying, rapid pyrolysis was conducted for the pretreated coals by using a free-fall pyrolyzer. This apparatus enables coal particles to be heated in a nitrogen stream at rates from 10^3 to 10^4 K/s depending on particle density and diameter. The temperature was 1253 K at the isothermal section of the reactor. The details of the apparatus were described elsewhere.⁶

To investigate the effect of macerals on sulfur-form and distribution, the samples were fractionated into three density groups by sink-float in zinc chloride aqueous solution. The separated samples were repeatedly washed to remove zinc chloride, which might catalyze tar decomposition. The absence of zinc chloride in the sample was confirmed by extraction with hydrochloric acid solution.⁹

Sulfur capture behavior was investigated for rapid pyrolysis char in hydrogen sulfide/nitrogen gas mixture at 1073 K in a fixed bed.

Some improvements to ASTM (D2492) were applied to analyzing sulfur forms (pyrite, ferrous sulfide, sulfate and organic sulfur) in parent and chemically pretreated coals, and in rapidly pyrolyzed char. The details of the analytical method were reported previously.¹⁰ Sulfur K-edge XANES was applied to specifying the forms of organic sulfur.¹¹ XANES measurements were carried out at beam line 2A of Photon Factory in the High Energy Accelerator Research Organization. Si(111) monochromators were used to vary the incident X-ray energy. The beam irradiated the samples fixed on a nickel plate under 10^{-3} Pa in a vacuum chamber. 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 with the assumption that the giant resonance of K_2SO_4 appears at 2481.7 eV. The third derivatives of XANES spectra from model compounds were used as fingerprints for interpreting sulfur forms in the sample. Pyrite, ferrous sulfide, crystalline sulfur, DL-cystine, thioxane-9-one, s-methyl-L-cysteine, DL-methionone sulfoxide and potassium sulfate were selected as the model compounds.

RESULTS AND DISCUSSION

Figure 1 shows change in organic sulfur content in rapid pyrolysis with the chemical pretreatments. A considerable decrease in organic sulfur was observed for rapid pyrolysis chars of nitric acid or potassium hydroxide pretreated Muswellbrook. Rapid pyrolysis of parent coal did not show appreciable change in organic sulfur. The effect of chemical pretreatments can also be found in the rapid pyrolysis of Illinois No.6 coal. The organic sulfur content decreased to one third of parent coal. While Mequinenza is well known as a lignite containing more than 10 % of organic sulfur, the rapid pyrolysis of this sample shows that about half of organic sulfur decomposes during the treatment. XANES spectra indicate large amount of disulfide in

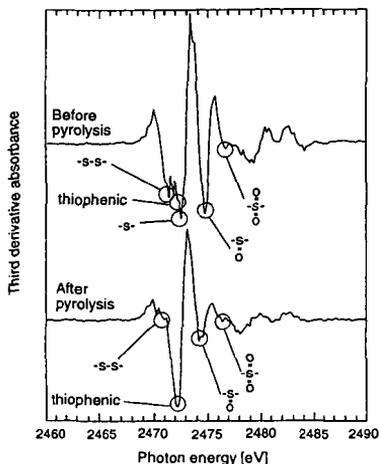


Fig.2 Sulfur K-edge XANES spectra of HNO_3 treated coal before and after pyrolysis.

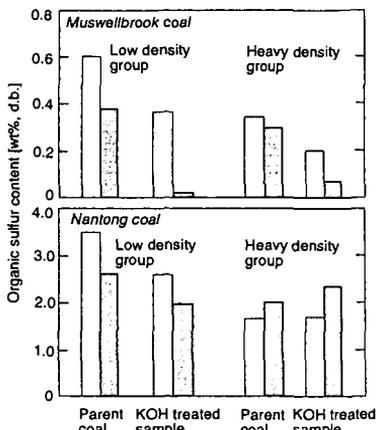


Fig.3 Effect of KOH pretreatment on organic sulfur content before and after pyrolysis for density separated samples. (\square , before pyrolysis; \square , after pyrolysis)

Mequenza coal which caused the high extent of organic sulfur removal during rapid pyrolysis. Efficient removal of organic sulfur was obtained for the combined process of rapid pyrolysis with nitric acid pretreatment. Potassium hydroxide pretreatment could not be carried out because lignite was dissolved with alkali solution.

Figure 2 shows third differential curves of XANES spectra for the nitric acid treated Illinois No.6 coal before and after rapid pyrolysis. Strong peaks are observed around 2472 eV for the coal before pyrolysis, which are attributable to disulfide, thiophene and sulfide. A strong peak at 2474.5 eV results from sulfoxide. This peak is larger than that of parent coal. After the rapid pyrolysis of nitric acid treated coal, the peaks of disulfide and sulfide disappear and the sulfoxide peak becomes small.

To investigate the effect of change in the forms and content of organic sulfur with maceral concentration on desulfurization behavior, potassium hydroxide pretreatment and rapid pyrolysis were conducted for the density separated coals of Muswellbrook and Nantong. The samples were separated into three groups (low, medium and heavy density groups): $<1.26 \text{ g/cm}^3$; $1.26\sim 1.40 \text{ g/cm}^3$; $>1.40 \text{ g/cm}^3$ for Muswellbrook, and $<1.32 \text{ g/cm}^3$; $1.32\sim 1.42 \text{ g/cm}^3$; $>1.42 \text{ g/cm}^3$ for Nantong coals, respectively. Figure 3 indicates change in organic sulfur content with potassium hydroxide pretreatment and rapid pyrolysis for the density separated coals. The clean char less than 0.02 % of organic sulfur was obtained for the potassium hydroxide treated sample of Muswellbrook low density group. While change in organic sulfur content was not appreciable after rapid pyrolysis of heavy density group, potassium hydroxide pretreatment was effective for change of the thermally stable organic sulfur to decomposable forms. For Nantong low density group, some extent of organic sulfur decreased with potassium hydroxide pretreatment and rapid pyrolysis. Organic sulfur content increased after rapid pyrolysis for heavy density group.

Figure 4 shows change in sulfur content of char exposed to a nitrogen stream containing hydrogen sulfide in a fixed bed at 1073 K. The sample char was obtained by rapid pyrolysis of Rosebud coal in a nitrogen stream at 1253 K. Sulfur content increased with hydrogen sulfide concentration and attained to 12 % in nitrogen gas containing 2.91 % of hydrogen sulfide. XANES analysis indicates that adsorbed sulfur formed organic sulfur in the solid phase.

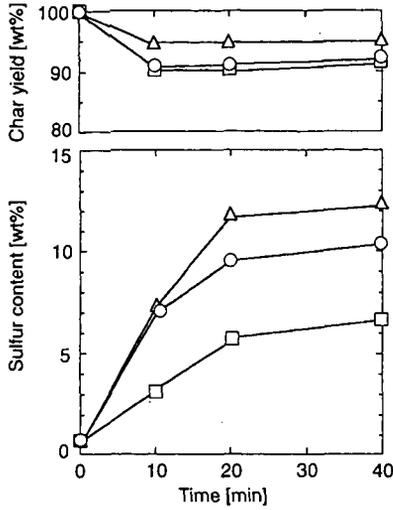


Fig. 4 Sulfur capture by Rosebud char in H₂S/N₂ stream at 1073 K. (Hydrogen sulfide conc.: □, 0.29%; ○, 1.01%; △, 2.91%)

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