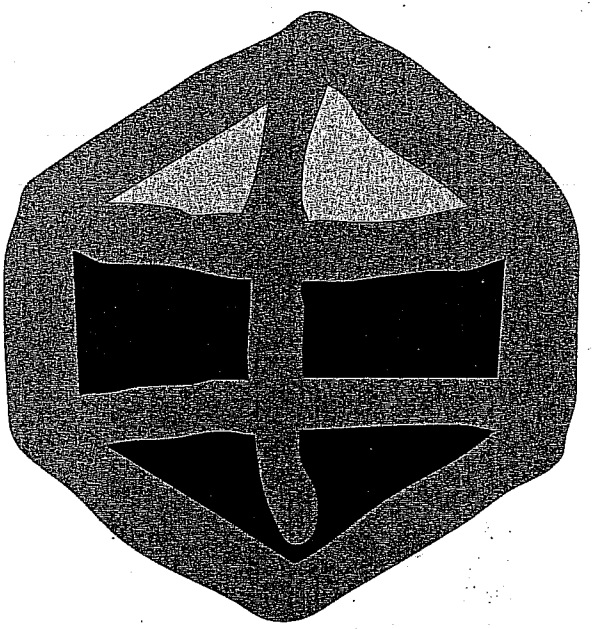
PROCEEDINGS



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XPS Investigation to Determine Nitrogen Functional Forms in Coals

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ABSTRACT

To measure nitrogen functional forms in coals by X-ray photoelectron spectroscopy (XPS), suitable operation conditions and analytical methods were discussed. A special polyimido film was employed to determine the accurate sensitivity factors of carbon 1s and nitrogen 1s. The peak widths of some nitrogen types were obtained to analyze the difference of normalized N1s spectrum between coals. Then a good correlation between N/C area ratio measured by XPS and bulk N/C atomic ratio was obtained for 50 coals and 7 model compounds.

Key words: X-ray photoelectron spectroscopy, nitrogen, technique

1. INTRODUCTION

For a comprehensive understanding of the effect of coal types on the formation of N_2O and NOx precursors, it is necessary to study nitrogen structure in coals. An X-ray photoelectron spectroscopy (XPS) is one of the non-destructive techniques that provide the identification of functional groups of carbon and nitrogen in coals. Much of work has been made with XPS in the quantification of organic nitrogen forms. However, a similar understanding of the chemistry of organically bound nitrogen in coal was not yet emerged [1]. The aim of the present work was to find a suitable operation condition of XPS on quantification of nitrogen forms and then to investigate a quantitative conclusion of the nitrogen functional forms by

using various ranks of coals and some nitrogen containing model compounds.

2. EXPERIMENTAL

2.1 Coals and model compounds

50 coals covering a wide range of rank from semi-anthracite to sub-bituminous coal were used in this experiment. The carbon content ranged from 72.41% to 89.72% and nitrogen content from 0.80% to 2.78% on a dry-ash-free basis. The formation type, molecular formula and carbon of the model compounds used in this study and nitrogen contents are given in Table 1.

Table 1: Model compounds used in the study

Name	Type	Molecular formula	C	N
			wt%	Wt%
Carbazole	Pyrrolic	$C_{12}H_9N$	86.23	8.38
Poly vinyl carbazole	Pyrrolic	$[C_{14}H_{12}N]_n$	86.60	7.22
Acridine	Pyridinic	$C_{13}H_8N$	87.15	8.72
2,2'-Biquinoline	Pyridinic	$C_{18}H_{12}N_2$	84.38	10.94
2-Amino pyridine	Pyridinic, Amino	$C_5H_6N_2$	63.80	29.77
5-Amino salicylic acid	Amino	$C_7H_7NO_3$	54.85	9.14
Poly acrylonitrile	Nitrile	$[C_3H_3N]_n$	67.92	26.42

Table 2: Standardization of parameters

Parameter		Suitable conditions
Surface roughness		Smooth surface by press
Particle size		Below 42 μ m
Pressure		Below 1×10^{-6} Pa
Inside diameter of slit		20.3 mm
X-ray	Power	300 W
	Irradiation time	Below 60 min.
	Number of scan	20 times
Etching		Nothing
Binding energy used by analysis		408.0-396.0 eV
Base line	Averaging values of	20 points around 396.0 and 408.0 eV
Smoothing	Savitzky-Golay	9 points
FWHM		Pyrrolic, Pyridinic and Quaternary: max. 2.3
		Nitrogen-oxide : 3.59

2.2 XPS measurement

X-ray photoelectron spectroscopy (Shimazu ESCA-K1) with Mg-K α non-monochromatic radiation was used to determine the functional forms of coal nitrogen. The spectrometer was run at pass energy of 32 eV with a step size of 0.05eV for nitrogen and 0.1eV for carbon. The other parameters examined in this study are shown in Table 2. To compensate for sample charging, all binding energies were referenced to carbon 1s at 285.0eV. The spectra are plotted as electron intensity versus binding energy.

3.RESULTS

3.1 Quantification of N(1s) spectrum

First, it is important to determine sensitivity factor in the XPS analyzer used for quantification of the spectra. A special polyimido film was employed to determine sensitivity factors for measurements of coals as a suitable synthesis material including carbon, nitrogen and oxygen. Nitrogen (1s) sensitivity factor 1.683 was obtained, when carbon sensitivity factor was 1.0, from C1s and N1s spectrum of polyimido as shown in Figure 1. Figure 2 shows comparison of the N/C area ratio by XPS and the bulk N/C atomic ratio for 50 different coals and 7 model compounds. It shows a good carbon linear correlation when integrating area includes broad shape-up peaks over high binding energy.

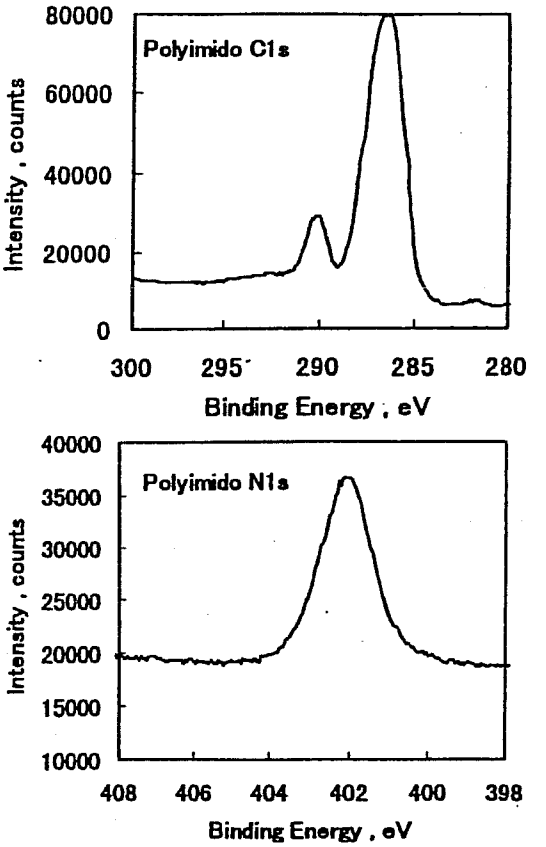

Figure 1: Carbon and nitrogen 1s spectrum of the polyimido film

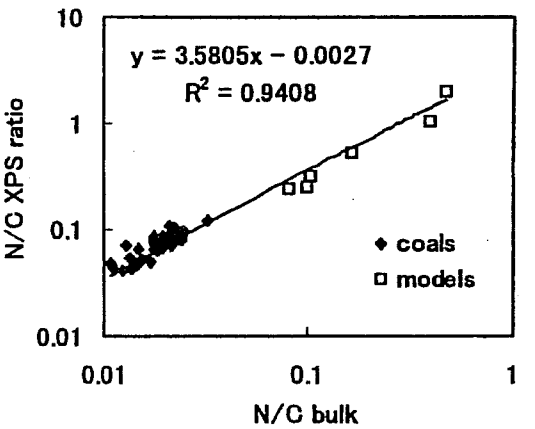

Figure 2: Comparison of the surface N/C area ratio by XPS and the bulk N/C atomic ratio

3.2 Determination of parameters to resolve N1s spectrum

Several investigators resolved using three peaks, pyrrolic, pyridinic, and quaternary nitrogen, to fit N1s spectra. It is well recognized that pyrrolic nitrogen is dominant species in various rank coals, however, effects of coal rank on distribution of nitrogen functional forms are obtained difference results. Kambara et al. reported that the content of pyrrolic nitrogen increased and pyridinic nitrogen decreased with increasing rank against other researcher results [2]. This reason was why the curve resolution results of complex N1s spectrum were affected by some parameters such as each peak position and peak width. It is necessary to determine some parameters accurately for quantification of nitrogen functionalities in coals.

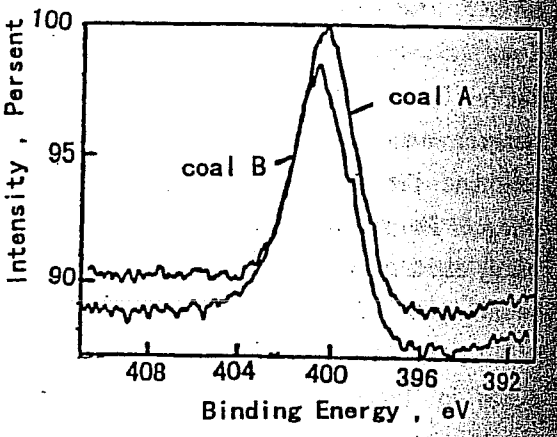

Figure 3: N1s spectrum of coal A and coal B

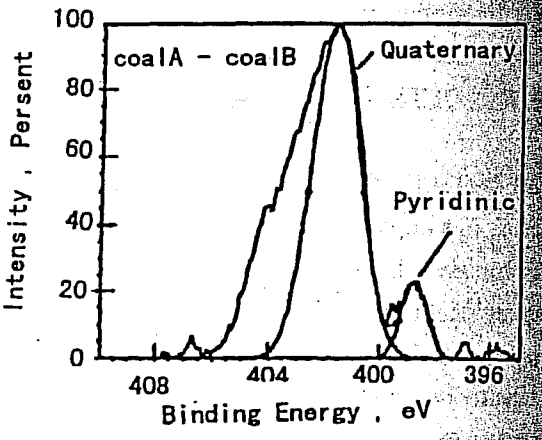

Figure 4: N1s spectra of coal A – coal B

There are two methodologies, use of model compound spectra or mathematical analysis by using many spectra of coals, to determine the parameters. Mathematical analyses are employed in this work because model compound spectra may not provide accurate parameters in heterogeneous structure of coals. Figure 3 shows N1s spectra of coal A (N%=1.63,C%=82.0, daf) and coal B (N%=1.62,C%=74.4, daf). Difference of normalized spectrum between coal A and coal B was the spectrum without pyrrolic nitrogen peak that resolved easily as shown in Figure 4. The most important parameter, the peak width, was obtained to examine the distribution of nitrogen forms accurately by the mathematical analysis.

REFERENCES

[1]Robert M Davidson; *Nitrogen in Coal, IEA Coal Research*, **1994**, 13

[2]Shinji Kambara et al.; *Energy & Fuels*, **1993**, 7, 1013-1020