Organic Oxygen and Nitrogen Transformations During Pyrolysis of Coal

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Abstract

The chemical changes in organically bound oxygen and nitrogen forms have been studied using X-ray Photoelectron Spectroscopy (XPS) following mild pyrolysis of Argonne Premium coal. The evolution of CO_2, CO and H_2O during pyrolysis was quantified and their appearance was associated with the loss of hydroxyl and carboxyl functional groups present in coal. There is a corresponding loss of quaternary nitrogen species upon pyrolysis. This loss of quaternary nitrogen species is interpreted to result from broken associations between pyridinic nitrogen and hydroxyl groups from either carboxylic acids or aromatic hydroxyl moieties.

I. Introduction

During the pyrolysis, hydropyrolysis and liquefaction of coal the thermolysis of labile chemical bonds is thought to initiate a complex series of reactions that can lead to either hydrogen addition reactions and lower molecular weight products or retrograde cross-linking reactions and heavier products [1-4]. The chemical reactions of organic oxygen functionalities initially present in coal have been implicated as important factors. However, there exists little detailed information about the transformations that take place early during coal conversion. The present work focuses on the chemical changes of organically bound oxygen and nitrogen forms in coal structure prior to the evolution of liquid-like products during coal pyrolysis.

II. Experimental

X-Ray Photoelectron Spectroscopy was used to speciate and characterize the organic oxygen and nitrogen functional group distributions. An energy correction was made to the spectra due to sample charging based on a carbon (1s) peak position of 284.8 eV. The amount of organic oxygen was determined relative to carbon from the total area of the XPS peaks after accounting for inorganic contributions to the oxygen (1s) and sulfur (2p) peak intensities [5-7]. The inelastic background and shake-up emission features to the carbon (1s) spectra were subtracted prior to curve resolution [8]. The details of the carbon (*1s*) and nitrogen (*1s*) curve resolution process appear elsewhere [5,6,8,9]. Argonne Premium coals were used in this study [10]. Pyrolysis experiments were done in helium. The details of the pyrolysis reactor have been described previously [5]. Briefly, a linear (0.5 deg/sec) heat-up period from 160 to 400°C was followed by isothermal reaction at 400°C for 5 min. Analysis of the accumulated gas composition following the heat-up and isothermal period was made by GC analysis using a thermal conductivity detector.

III. Results and Discussion

During the early stages of coal pyrolysis a substantial amount CO, CO_2 H_2O and other light gaseous products are formed. The amount of these gaseous products have been quantified. Table I shows the results of gas analyses following pyrolysis at 400°C for 5 min. The results are expressed as molecules per 100 carbons initially present in each coal sample. Included in Table I is the total amount of oxygen that can be accounted for by these gaseous products. For the lower rank coals the loss of oxygen is greater than for higher rank coals.

XPS has been used to follow the corresponding changes in total organic oxygen in the coal chars. Table II shows the results expressed as atoms of oxygen per 100 carbons initially present. Included in Table II are the corresponding results of the XPS analysis of fresh Argonne premium coals. All coals show a decrease in the level of organic oxygen upon pyrolysis but the effect is most evident with lower rank coal.

There are well known problems associated with different techniques for establishing the level of total organic oxygen and different oxygen functionalities present in coal. Fast neutron activation analysis (FNAA) for oxygen analysis [11,12] followed by correction for inorganic forms has been attempted as an alternate to ASTM oxygen-by-difference estimates and similar modified "by difference" formulas. Indirect chemical methods have been combined with these by-difference determinations for total oxygen to provide functional group information [13, 20, 21]. These results have been compared to indirect pyrolysis attempts at organic oxygen analysis [13, 22]. ^{13}C NMR analysis of Argonne Premium coal has yielded insight into the kinds of organic functionalities present [14]. XPS has also been used to evaluate organic oxygen [5, 15-19].

With the emergence of more reliable methods for determining XPS shake-up and inelastic loss processes, the XPS carbon (1s) line shape can provide quantitative information about the kinds of organic oxygen functionalities initially present in coal [8]. XPS was used in the present work to determine the kinds of organic oxygen functionalities initially present in Argonne Premium coals and those that remain after pyrolysis. Figure 1 shows the XPS carbon (1s) spectrum following background subtraction of the initial Wyodak. Included in this figure are the results of a curve resolution analysis. For the starting Wyodak coal, the main peak is due to unoxidized carbon. There is also a strong peak due to carbon with a single bond to oxygen. Carbonyl and carboxyl peaks show up with less intensity. After pyrolysis, only singly bonded carbon oxygen functionalities are observed and with less relative intensity to unoxidized carbon species. The digital results of the detailed XPS analysis for oxygen functionality for Wyodak and the other Argonne Premium coals are shown in Table II. Low rank coals contain much more carbonyl and carboxyl species. After pyrolysis, low rank coals show a loss of carboxyl and carbonyl species. For low rank coals, much of the lost carboxyl and carbonyl oxygen functionalities can be accounted for in the evolution of light gaseous products. The loss of hydroxyls, mostly from acid functional groups, is thought to occur and explains the appearance of H_2O as a major pyrolysis product of low rank coal.

The changes in the XPS nitrogen (1s) line shape following mild pyrolysis of Argonne Premium coal have been studied. These results are shown in Table III. In contrast to oxygen, the total level of nitrogen remains nearly constant relative to carbon after pyrolysis [9]. The retention of nitrogen in the pyrolysis char is expected, based on lack of gaseous evolution of nitrogen containing pyrolysis products. The results of curve resolution analysis of the nitrogen (1s) spectra for fresh Argonne Premium coals have been previously reported [9] and these results are included in Table III for comparison. In all cases the level of quaternary nitrogen decreases upon pyrolysis, while a corresponding increase in pyridinic nitrogen is observed. The level of pyrrolic nitrogen remains almost constant. These observations, taken together with the results for organic oxygen, suggest that the quaternary nitrogen species are pyridinic forms associated with hydroxyls and that the association is broken as a result of thermal reactions [9].

IV. References

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Table I

	Molecules Per 100 Initial Carbons				
Coal	CH_4	CO_2	H_2O	CO	Total Oxygen in These Gases
Beulah Zap	0.26	1.58	4.07	0.21	7.44
Wyodak	0.20	0.84	3.30	0.40	5.38
Illinois #6	0.40	0.32	0.56	0.05	1.25
Blind Canyon	0.33	0.22	0.54	0.08	1.06
Pittsburgh #8	0.44	0.56	0.34	<0.05	1.46
Lewiston	0.46	0.11	0.19	<0.05	0.41
Upper Freeport	0.09	0.06	0.12	<0.05	0.24
Pocahontas	0.05	0.05	0.10	<0.05	0.20

Table II

Coal		Atoms Per 100 Initial Carbons: Total Org. Oxygen	-O	C=O	O-C=O
Beulah Zap	Fresh	18.8	11.2	1.4	6.2
	Char	10.7	9.2	0.5	1.0
Wyodak	Fresh	16.9	10.4	1.3	5.2
	Char	10.8	9.3	0.5	1.0
Illinois #6	Fresh	10.9	9.9	0.4	0.6
	Char	8.2	8.2	0.0	0.0
Blind Canyon	Fresh	10.0	9.6	0.4	0.0
	Char	8.5	8.5	0.0	0.0
Pittsburgh #8	Fresh	7.8	6.8	0.9	0.0
	Char	6.2	6.2	0.0	0.0
Lewiston	Fresh	8.0	6.8	1.2	0.0
	Char	6.5	6.5	0.0	0.0
Upper Freeport	Fresh	4.5	3.9	0.6	0.0
	Char	3.8	3.8	0.0	0.0
Pocahontas	Fresh	3.2	3.2	0.0	0.0
	Char	3.0	3.0	0.0	0.0

Table III

Coal		XPS Mole Percent (± 3.0): Pyridinic	Pyrrolic	Quaternary
Beulah Zap	Fresh	26	58	16
	Char	29	60	11
Wyodak	Fresh	25	60	15
	Char	30	61	9
Illinois #6	Fresh	26	62	12
	Char	30	63	7
Blind Canyon	Fresh	31	55	14
	Char	39	57	4
Pittsburgh #8	Fresh	32	61	7
	Char	35	63	2
Lewiston	Fresh	31	60	9
	Char	34	63	3
Upper Freeport	Fresh	28	65	7
	Char	35	63	2
Pocahontas	Fresh	33	64	3
	Char	34	65	1

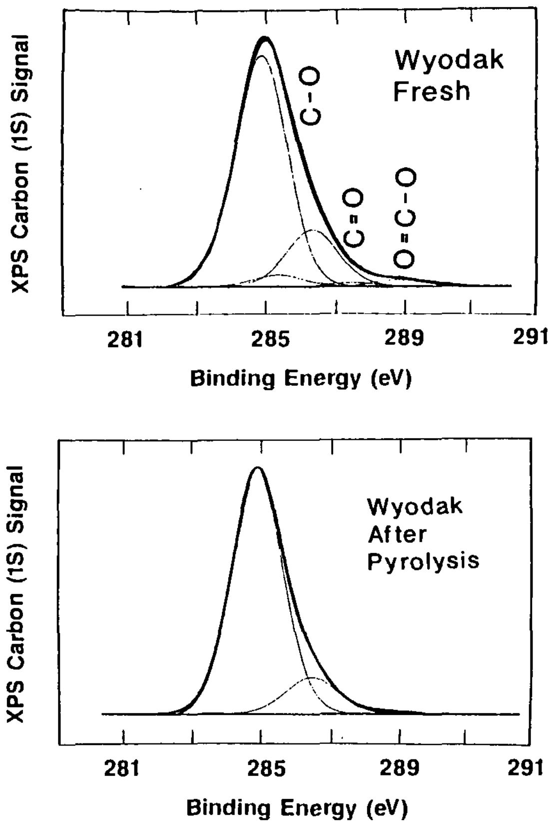

Figure 1

Top) XPS carbon (1s) spectrum of fresh Wyodak coal after background subtraction. Included in the figure are the results of the curve resolution analysis. Bottom) XPS carbon (1s) spectrum after background subtraction of Wyodak coal pyrolyzed at 400 Celcius. Included in the figure are the results of curve resolution analysis.