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XPS Analysis of Surface Texture of Coking Coal in Fenxi County†

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With the adoption of XPS method, this paper is aimed at the research into the surface texture of the sample coal of Fenxi county, with the outcome as follows. There is a low content of nitrogen and carbonyl and carboxyl in the coal,with carbon mainly existing in the form of C-C. Most oxygen in the coal exists in the form of phenolic hydroxyl and ether oxygen.In organic sulphur constitutes a small percentage in the coal, with organic sulphur,in the three major forms of (sub) sulfone, thiophene and thiol (ether).

Keywords: XPS, Coking coal, Surface texture.

INTRODUCTION

The coking coal, a kind of scarce coal, accounts for only one fourth of all the coal resources in China. The coal mine of Fenxi and other 8 mines in Shanxi Province (China) possess the largest reserve of coking coal, with recoverable reserves accounting for roughly half of the total nationwide[1]. Over the years, the high content of sulphur in the coal has been mainly responsible for the delayed comprehensive use. The occurrence of oxygen in the coal has been a key research area of the coal texture. As oxygen is the most abundant hetero-atom in the coal, the form of the functional groups of C-O makes a major difference to coal nature, with the existence of organic oxygen bearing close relation to carbon in the coal. The analysis of the surface texture and research into the occurrence of the major elements in the coal will be of great significance to the deprivation of what is not needed in the coal, the improvement of the comprehensive utilization of the coal, as well as conservation and recovery of scarce coking coal resources.

As one of the most effective methods of element analysis arising in recent years and with a possession of a high recognition capacity of chemical characteristics of material surface and no damage of sample textures, X-ray photoelectron spectrum (XPS) can be used to analyze the existing elements in samples and check in a direct way the existing form of these elements, leading to its wide application in the research into coal surface texture. Beamson, Briggs, Yu, Wu and other professionals have conducted research into the fundamentals and technology of XPS[2-4]. Other several professionals[5-9] have carried out the research into the occurrence of oxygen and carbon in the coal. Chenpeng, Dai Shifeng, Liu Yanhua, Urban, Vdovenkova and other professionals have completed the analysis of the existing forms of sulphur in the coal[10-14]. Zhu and Zheng[15] have conducted the research into the analysis method of XPS applied in the form of sulphur in the washed coal for coal making, with a discussion into the methods of separating and fitting used in the XPS spectrums. Chang *et al.*[16] have made a correlation analysis of surface texture of microscopic groups of coal with varying degree of reduction[16]. Yang in collaboration with his colleagues, carried out research into photochemical and oxygenated XPS into different levels of density components of coal in Shenfu Coalmine[17]. Liu Fenrong and other professionals have researched into the changes involving functional groups and migrating activities of sulphur in the coal surface[18].

The research into, with the adoption of XPS, the surface texture and migrating regularities in the coal at home abroad has been mainly involved in the low-content coal, with no report on the research into the surface structure of high-sulphur coking coal, especially the crude coal in Fenxi County. On the basis of accomplished XPS analysis of surface texture of coking coal in Fenxi County by other professionals, this paper tries to reveal the existing shape of major elements in the coal.

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TABLE-1
INDUSTRIAL AND ELEMENT ANALYSIS OF THE SAMPLE

Industrial analysis (%)				Element analysis (%)				
Mad	Vd	Ad	FCd	Cdaf	Hdaf	Ndaf	St,d	Odaf
1.03	27.81	18.02	54.17	84.21	4.45	1.52	2.68	6.55

EXPERIMENTAL

With 200-mesh screen, the sample of broken and ground 5 g coal, is taken from Xinyu Coal Washery affiliated with Fenxi Mining Group and kept under seal. The industrial and elemental analysis of the sample is shown in Table-1.

With the use of X-ray photoelectron spectrograph of hermo ESCALAB 250, with the X-ray source of mono-colour Al Ka (hv =1486.6 eV), the power of 150W, the beam spot of 500 μm the experiment and the fixed penetration capacity of energy analysis of 30 eV, is completed in the Analysis & Test Center Affiliated with China University of Science & Technology of China, with C1s (284.6 eV) as the scaling standard for adjustment. With the fitting method of XPS peak, the spectrum is obtained. With the help of XPS peak fitting method to fit the spectrum, this paper, in accordance with relevant documents to determine the binding energy position of functional group, makes an effort. After the analysis and process of relevant data, to acquire the shape information of elements in the coal.

RESULTS AND DISCUSSION

Full graphic analysis of XPS: The XPS spectrum in the sample coal is shown in Fig. 1. Due to the small quality fraction of N in the sample, there are just peaks of O, C, S and Si in the spectrum. The corresponding peak scope, peak position, half-peak width and relative quality fraction in Fig. 1 are shown in Table-2.

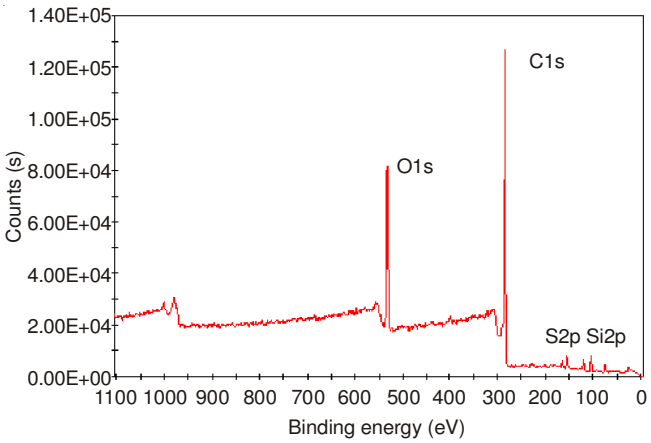

Fig. 1. XPS spectrum in the sample coal

TABLE-2
DISTRIBUTION OF DIFFERENT ELEMENTS IN THE SAMPLE COAL

Name	Start E (eV)	Center E (eV)	End E (eV)	FWHM (eV)	At. (%)
C1s	294.25	284.58	281.85	1.32	79.62
S2p	173.2	163.81	160.9	1.16	2.63
O1s	536.6	532.82	528.95	2.18	14.2
Si2p	107.55	103.53	99.95	2.01	3.55

Occurrence of carbon in the surface texture of coal: With the separating and fitting of carbon spectrum, the best effect is shown in Fig. 2. With a reference to the research achievement made by Luo Yunfei, Duan Xuqin and other professionals in the occurrence of coal surface carbon, the scope of electronic binding energy is as follows: the peak near 290.0 eV falls into carboxyl (COO-), the peak of 287-288 eV falls into carbonyl (C=O), the peak near 286.5 eV falls into phenol carbon or ether carbon (C-O) and the peak around 285.0 eV falls into aroma unit and its substitute for paraffin (C-C, C-H), respectively.

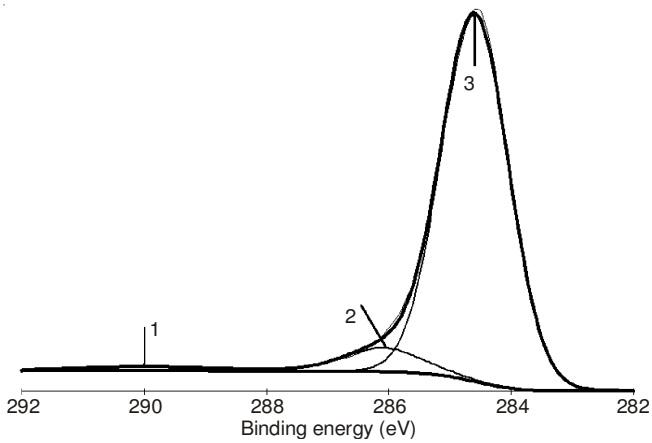

Fig. 2. XPS fitting spectrum of C1s

There are three peaks in Fig. 2. In accordance with the position of binding energy, three attribution groups of carbon are determined, with the calculation of relative content made in line with the peak areas. The binding energy position, peak attribution group, peak number and relative content shall be referred to what is shown in Table-3.

TABLE-3
PEAK ATTRIBUTION AND RELATIVE CONTENT OF THE CARBON IN THE SAMPLE COAL

XPS type	Peak number	Attribution group	Binding energy position	Content (%)
C1s	1	O=C-O	290.00	2.00
	2	C-O	286.10	7.58
	3	C-C, C-H	284.60	90.42

The content of carbonyl is rather low despite its wide distribution in the coal, from peat cube to anthracite coal. It exists largely in the form of quinonyl in high-coalification coal. Carbonyl occurs in peat cube, bovey coal and weathered coal, but hardly exist in bituminous coal. It can be discovered from that there is no attribute peak within the scope of 287-288 eV, with the indication in the sample coal of virtually zero content of carbonyl (C=O) and the content of 2.00 % carboxyl revealing high coalification (Table-3). C-C constitutes the majority to show a high percentage of alkyl lateral chain in the sample coal.

Occurrence shape of oxygen in the coal surface texture: XPS fitting spectrum of the sample coal with three peaks in Fenxi County is shown in Fig. 3. The three positions of binding energy are 533.60, 532.75 and 531.60 eV, respectively. A research into the occurrence shape of oxygen in the coal surface texture through XPS has also established the fact of controversy with regard to electronic binding energy of attribute peak and attribution group. 532.75 eV is defined as the mono-key attribute peak of carbon oxygen (C-O) in this research for two reasons. For one, its position of binding energy is different from the research outcome by Xuqing and Zhiyuan[7,17], with peak displacement within the acceptable scope. For another, mono-key carbon oxygen is the major existence form of organic oxygen in the coal, with the support of the analysis outcome in a mutual way.

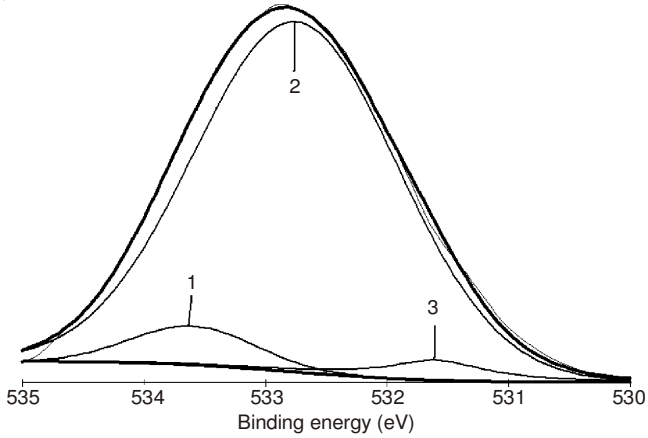

Fig. 3. XPS fitting spectrum of O1s

According to the data displayed in Table-4, the content of mono-key carbon oxygen in the coal is 90.09 %, which is in agreement with the fact that there is a high content of hydroxyl in the coal, with an overwhelming majority of phenolic hydroxyl and ether oxygen and an extreme minority of alcohol hydroxyl[16,19].

TABLE-4
OXYGEN ATTRIBUTION AND RELATIVE CONTENT OF THE CARBON IN THE SAMPLE COAL

XPS Type	Peak number	Attribution group	Binding energy position	Content (%)
O1s	1	O=C-O	533.60	6.04
	2	C-O	532.75	90.09
	3	C=O	531.60	3.87

Occurrence shape of sulphur in the coal texture: In the analysis the shape of coal sulphur with the use of XPS, it is generally acknowledged that there are four classifications of coal sulphur, *i.e.*, sulphide (alcohol), thiophene, sulfones and inorganic sulphur, with the distribution scope of electronic binding energy as 162.2-164, 164-164.4, 165-168 and 169-171 eV[15]. XPS fitting spectrum of S2p is shown in Fig. 4, from which we can discover 5 peaks, with the attribution groups and their respective content referred to Table-5.

From the data shown in Table-5, we have known that the content of inorganic sulphur is 7.56 %, with the conclusion of its low content in the sample coal, which, as a kind of medium-and-high sulphur coal, has organic sulphur as its sulphur-bearing group, with the content of 23.67 % thiophene characterized as stable and difficult to deprive. Thio-alcohol, with a percentage of 50 %, has the highest content in the organic group.

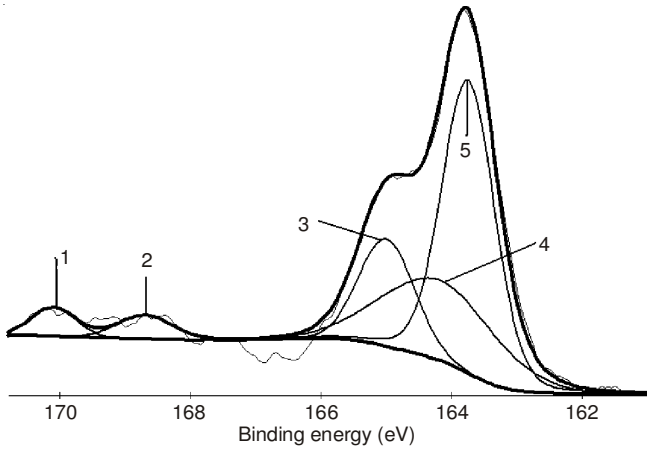

Fig. 4. XPS fitting spectrum of S2p

TABLE-5
SULPHUR ATTRIBUTION AND RELATIVE CONTENT OF THE CARBON IN THE SAMPLE COAL

XPS Type	Peak No.	Attribution group	Binding energy position	Content (%)
S2p	1	Inorganic sulphur	170.20	3.77
	2	Inorganic sulphur	168.70	3.79
	3	(sub) sulphone	165.00	17.35
	4	Thiophene	164.10	26.67
	5	Thio-alcohol(ether)	163.70	48.42

Conclusion

There is an extremely low content of nitrogen in the sample coal in Fenxi County, with no attribute peak of N in XPS check. Alkyl lateral chain is abundant in the sample. Key C-C is the main existing form of carbon in the coal, with C-C and C-H accounting for 90 %. The content of mono-key carbon oxygen (C-O), the main existing form of organic oxygen, is 90.09. Carboxyl (O=C-O) has an extremely content and that of carbonyl (C=O) is even less, almost zero. The coking coal in Fenxi County has a low content of inorganic sulphur and a major content of organic sulphur. It falls into medium-and-high sulphur coal. The content of respective groups in the organic sulphur in a high-low order is thio-alcohol (ether), thiophene and (sub) sulfone, with the first item accounting for 48.42 %.

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