

### 高硫煤镜质组热解过程中结构变化及有机硫形态变迁规律研究

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### Structure change and organic sulfur forms transformation during pyrolysis of high-sulfur vitrinite

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**摘要** 用手选富集与离心分离相结合的方法, 从两种全硫含量相近的新西兰煤(NXL;  $S_{t, ad}=1.84\%$ )和山西煤(SX;  $S_{t, ad}=1.80\%$ )中分离出高纯度镜质组。在高纯Ar气氛下, 分别制备了300、500、700和1 000 °C下的镜质组焦。用FT-IR研究了两种镜质组中的脂肪氢、芳香氢随温度的变化, 结果表明, SX镜质组中脂肪氢的相对含量较高, 在热解过程中活性高于同温度下的NXL镜质组; 两种镜质组中的脂肪氢相对含量都随温度升高而降低, 温度高于500 °C时, SX镜质组中脂肪氢相对含量基本不变, 当温度高于700 °C时, NXL镜质组中的脂肪氢相对含量基本保持不变; 热解过程芳香氢都表现出先增大后减小的趋势。用XPS研究了镜质组中的有机硫含量及形态随温度的变化, 结果表明, SX镜质组中易分解的有机硫化物较多, 在300 °C以下即可分解完全; NXL镜质组中的有机硫化物分解完全在700 °C左右, 两种镜质组中的噻吩类硫的含量都随热解温度的升高而增加, 砷类硫的含量随热解温度的升高而降低。

**关键词:** 镜质组 有机硫变迁 热解 FT-IR XPS

**Abstract:** High purity vitrinite was separated and concentrated from New Zealand(NXL;  $S_{t, ad}=1.84\%$ ) and Shanxi(SX;  $S_{t, ad}=1.80\%$ ) coal which have similar sulfur content. The vitrinite was pyrolyzed in a tube furnace reactor under argon at 300, 500, 700 and 1 000 °C. The effect of temperature on the functional group content and organic sulfur forms transformation was examined by Fourier transform infrared spectrum and X-ray photoelectron spectrum, respectively. The FT-IR experiments show that aliphatic hydrogen content in SX vitrinite and its reactivity is higher than those of NXL vitrinite at same temperature. The aliphatic hydrogen in both vitrinites decreases with increasing temperature. The aliphatic hydrogen content in SX and NXL vitrinite is unchanged when the temperature is above 500 and 700 °C, respectively. The aromatic hydrogen increases first and then decreases with increasing temperature. The XPS results show that the organic sulphide, which is more thermal unstable, is richer on surface of SX vitrinite than that of NXL. It is decomposed completely below 300 and 700 °C for SX and NXL, respectively. The content of thiophenic compounds increases with increasing temperature, but that of sulfones compounds is just the reverse.

**Key words:** vitrinite organic sulfur transformation pyrolysis FT-IR XPS

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- [1] 周师庸, 赵俊国. 炼焦煤性质与高炉焦炭质量[M]. 北京: 冶金工业出版社, 2008: 36-37. (ZHOU Shi-yong, ZHAO Jun-guo. Properties of coking coal and quality of coke for the blast furnace[M]. Beijing: Metallurgical Industry Press, 2008: 36-37.)
- [2] 孙成功, 李保庆. 煤中有机硫形态结构和热解过程硫变迁特性的研究[J]. 燃料化学学报, 1997, 25(4): 358-362. (SUN Cheng-gong, LI Bao-qing. Characterization of organic sulfur forms in some Chinese coals by high pressure TPR and sulfur transfer during hydrolysis[J]. Journal of Fuel Chemistry and Technology, 1997, 25(4): 358-362.)
- [3] 陈鹏. 用XPS研究兖州煤各显微组分中有机硫存在形态[J]. 燃料化学学报, 1997, 25(3): 238-241. (CHEN Peng. Application of XPS in study forms of organic sulfur in macerals of Yanzhou coal[J]. Journal of Fuel Chemistry and Technology, 1997, 25(3): 238-241.)
- [4] 张代林, 李伟锋, 曾涛, 郑明东, 王培珍. 炼焦煤的热解过程研究[J]. 煤炭学报, 2012, 37(2): 323-327. (ZHANG Dai-lin, LI Wei-feng, ZENG Tao, ZHENG Ming-dong, WANG Pei-zhen. Study on pyrolyzing process of coking coals[J]. Journal of China Coal Society, 2012, 37(2): 323-327.)
- [5] KELEMEN S R, GORBATY M L, GEORGE G N, KWIAK P J, SANSONE M. Thermal reactivity of sulphur forms in coal[J]. Fuel, 1991, 70(3): 396-402. 
- [6] WALKER R, MASTALERZ M. Functional group and individual maceral chemistry of high volatile bituminous coals from southern Indiana: Controls on coking[J]. Int J Coal Geol, 2004, 58(3): 181-191. 
- [7] PIETRZAK R, GRZYBEK T, WACHOWSKA H. XPS study of pyrite-free coals subjected to different oxidizing agents[J]. Fuel, 2007, 86(16): 2616-2624. 
- [8] KELEMEN S R, GEORGE G N, GORBATY M L. Direct determination and quantification of sulphur forms in heavy petroleum and coals: 1. The X-ray photoelectron spectroscopy (XPS) approach[J]. Fuel, 1990, 69(8): 939-944. 
- [9] KOZLOWSKI M. XPS study of reductively and non-reductively modified coals[J]. Fuel, 2004, 83(3): 259-265. 
- [10] CERNY J. Structural dependence of CH bond absorptivities and consequences for FT-IR analysis of coals[J]. Fuel, 1996, 75(11): 1301-1306. 
- [11] IBARRA J V, BONET A J, MOLINER R. Release of volatile sulfur compounds during low temperature pyrolysis of coal[J]. Fuel, 1994, 73(6): 933-939. 
- [12] MACHNIKOWSKA H, KRZTON A, MACHNIKOWSKI J. The characterization of coal macerals by diffuse reflectance infrared spectroscopy[J]. Fuel, 2002, 81(2): 245-252. 
- [13] 常海洲, 曾凡桂, 李文英, 李军, 贾建波, 谢克昌. 西北地区侏罗纪煤显微组分结构的Micro-FTIR研究[J]. 光谱学与光谱分析, 2008, 28(7): 1535-1538. (CHANG Hai-zhou, ZENG Fan-gui, LI Wen-ying, LI Jun, JIA Jian-bo, XIE Ke-chang. Micro-FTIR study on structure of macerals from Jurassic coals in northwestern China[J]. Spectroscopy and Spectral Analysis, 2008, 28(7): 1535-1538.)
- [14] WANG M J, HU Y F, WANG J C, CHANG L P, WANG H. Transformation of sulfur during pyrolysis of inertinite-rich coals and correlation with their characteristics[J]. J Anal Appl Pyrolysis, 2013, 104: 585-592. 
- [15] BROWN J R, KASRAI M, BANCROFT G M, TAN K H, GHEN J M. Direct identification of organic sulphur species in Rasa coal from sulphur L-edge X-ray absorption near-edge spectra[J]. Fuel, 1992, 71(6): 649-653. 
- [16] PIETRZAK R, WACHOWSKA H. The influence of oxidation with HNO<sub>3</sub> on the surface composition of high-sulphur coals: XPS study[J]. Fuel Process Technol, 2006, 87(11): 1021-1029. 
- [17] MARINOV S P, TYULIEV G, STEFANOVA M, CARLEER R, YPERMAN J. Low rank coals sulphur functionality study by AP-TPR/TPO coupled with MS and potentiometric detection and by XPS[J]. Fuel Process Technol, 2004, 85(4): 267-277. 
- [18] 闫金定. 炭载含硫化物热解行为的研究[D]. 太原: 中国科学院山西煤炭化学研究所, 2005. (YAN Jin-ding. Behavior of sulfur transformation during pyrolysis of sulfur model compounds on carbon support[D]. Taiyuan: Institute of Coal Chemistry, Chinese Academy of Sciences, 2005.)
- [19] 刘艳华. 煤中氮/硫的赋存形态及其变迁规律研究[D]. 西安: 西安交通大学, 2002. (LIU Yan-hua. An investigation on the forms and the fates of coal nitrogen/sulfur functionalities[D]. Xi'an: Xi'an Jiaotong University, 2002.)
- [20] HU H Q, ZHOU Q, ZHU S W, MEYER B, KRZACK S, CHEN G H. Product distribution and sulfur behavior in coal pyrolysis[J]. Fuel Process Technol, 2004, 85(8/10): 849-861. 
- [21] LIU F R, LI W, CHEN H K, LI B Q. Uneven distribution of sulfurs and their transformation during coal pyrolysis[J]. Fuel, 2007, 86(3): 360-366. 

- [1] 韩峰, 张衍国, 蒙爱红, 李清海. 水城褐煤热解的气体产物析出特征及甲烷的生成反应类型研究[J]. 燃料化学学报, 2014, 42(01): 7-12.
- [2] 董勇, 喻敏, 王鹏, 张梦泽, 睢辉, 崔琳, 张立强, 徐夕仁, 马春元.  $\text{CaCl}_2$ 添加对热解煤中汞析出规律影响的实验研究[J]. 燃料化学学报, 2014, 42(01): 31-36.
- [3] 柏静儒, 李晓航, 张亮, 贾春霞, 王擎. 柳树河油页岩微波干燥及其对热解特性的影响[J]. 燃料化学学报, 2014, 42(01): 37-42.
- [4] 武景丽, 陈天举, 罗希韬, 杨静, 王志奇, 吴晋沪, 孙立. 典型城市固体废弃物热解动力学机理研究[J]. 燃料化学学报, 2014, 42(01): 43-47.
- [5] 钟梅, 马风云. 不同气氛下煤连续热解产物的分配规律及产品品质分析[J]. 燃料化学学报, 2013, 41(12): 1427-1436.
- [6] 黄鑫, 张书, 林雄超, 王永刚, 徐敏. 低温加压热解脱氧对胜利褐煤亲水性的影响[J]. 燃料化学学报, 2013, 41(12): 1409-1414.
- [7] 孔娇, 程柱, 董洁, 焦海丽, 李凡. 平朔煤热解过程中PAHs的释放特性[J]. 燃料化学学报, 2013, 41(11): 1281-1286.
- [8] 张俊姣, 廖航涛, 陆强, 张阳, 董长青. 果糖低温快速热解制备糠醛的机理研究[J]. 燃料化学学报, 2013, 41(11): 1303-1309.
- [9] 李梅, 杨俊和, 张启锋, 常海洲, 孙慧. 用XPS研究新西兰高硫煤热解过程中氮、硫官能团的转变规律[J]. 燃料化学学报, 2013, 41(11): 1287-1293.
- [10] 张书, 白艳萍, 米亮, 郑盼盼, 陈绪军, 许德平, 王永刚. 升温速率对胜利褐煤热解过程中N迁移转化的影响[J]. 燃料化学学报, 2013, 41(10): 1153-1159.
- [11] 张晋玲, 王美君, 陈望舒, 付春慧, 任秀荣, 常丽萍. 逐级酸处理对锡盟褐煤的结构及热解特性的影响: 气相产物的生成[J]. 燃料化学学报, 2013, 41(10): 1160-1165.
- [12] 陆强, 廖航涛, 张阳, 张俊姣, 董长青. 果糖低温快速热解制备5-羟甲基糠醛的机理研究[J]. 燃料化学学报, 2013, 41(09): 1070-1076.
- [13] 邓靖, 李文英, 李晓红, 喻长连, 冯杰, 郭小汾. 橄榄石基固体热载体影响褐煤热解产物分布的分析[J]. 燃料化学学报, 2013, 41(08): 937-942.
- [14] 武宏香, 李海滨, 冯宜鹏, 王小波, 赵增立, 何方. 钾元素对生物质主要组分热解特性的影响[J]. 燃料化学学报, 2013, 41(08): 950-957.
- [15] 朱锡锋, 朱昌朋. 生物质热解液化与美拉德反应[J]. 燃料化学学报, 2013, 41(08): 911-916.