

CHARACTERIZATION STUDY OF COAL SPONTANEOUS COMBUSTION BY EPR SPECTROSCOPY

Munkhtsetseg Sambuu¹, Maria Cristina Mozzati²,
Pietro Galinetto², Erdene-Ochir Ganbold¹

¹*National University of Mongolia, Ulaanbaatar, Mongolia, munkhtsetseg_s@num.edu.mn*

²*Dipartimento di Fisica, University of Pavia, Pavia, Italy*

Annotation. In the present paper the low temperature treatment (up to 200 °C) of the coal was examined by the EPR, using 6,2 and 1,86 mW microwave radiation. During the heat treatment the formation of intermediate radicals has been revealed.

INTRODUCTION

Coals are actively interacting with oxygen and halogens. The reaction of coal with atmospheric oxygen or an adsorption of water molecules on its surface may appear at room temperature causing self-oxidation described as a spontaneous combustion of coal.

The heat treated coal goes through a decomposition of the organic substances (pyrolysis), giving rise to the existence of temporary fragments of molecules or free radicals [1]. The formation of free radicals during heating of coal was quite early considered and discussed by many authors [2–5]. Free radicals that formed by bond cleavage are the main intermediates during coal pyrolysis. Thus the determination of characteristics of these radicals becomes as highly important as the reaction itself in the thermal decomposition or in the study of mechanism of compound evolution.

Free radicals can be detected by EPR method if they are maintained at steady-state. Among the method advantages are included high sensitivity, non destructivity, minor dosage and broad detection in the study of free radicals in coals.

In the present paper the low temperature (up to 200 °C) treatment to the coal was examined by the EPR spectroscopy.

EXPERIMENTAL

Sample preparation

Coal sample description, preparation and its elemental analysis results are taken from [6]. Coal samples from Baganuur (abbreviated as Ba), Nalaikh (as Na), Sharyn-Gol (as ShG), Khotgor (as Kho), Khartarvagatai (as KhT) and Tavantolgoi (as TT) were chosen in the current work.

Sample mass is measured on the Ohaus explorer E10640 micro balance and sample size on Konus #5420 Diamond Stereomicroscope with 20×–40× magnification.

Heat treatment of coal and EPR measurements

The heat treatment of coal up to 200 °C was done, directly in the EPR spectrometer resonator.

After temperature treatment up to 200 °C, each coal sample was cooled directly in the resonator and measured the EPR spectrum at room temperature afterwards.

EPR measurement was performed at about 9,4 GHz with a Bruker spectrometer equipped with continuous nitrogen flow cryostat to study temperature dependence from room temperature (20 °C) up to 200 °C.

Solid samples were sealed directly into glass tubes (with mass of approximately 10–30 mg) and measured firstly in wide range of sweep field (~ 5000 Gs) and then central resonance field repeatedly. Each coal sample was kept at that exact temperature for 20 mins. EPR spectra were then registered every 50 °C. For every coal sample a signal at room temperature was also registered when cooled from 200 °C, approximately after 30 mins.

To the estimated value of the radical concentration of the coals at different temperature the correction was made by using the concentration of a reference sample (pitch, $g = 2,0028$ and $N_{ref} = 6,06 \times 10^{15}$ spin) measured at room temperature by applying the Boltzmann distribution of radicals between ground and excited states according to (1):

$$I_{abs} = \frac{N_{abs}}{m_{sample}} = \frac{N_{ref}}{m_{sample}} \cdot \frac{(T_{sample} - \theta_{sample})I_{sample}}{(T_{ref} - \theta_{ref})I_{ref}}, \quad (1)$$

where I_{sample} and I_{ref} are the sample and reference-signal intensity, respectively, T is the temperature under which the experiment was conducted, N is the number of radicals, and m_{sample} is the sample mass. The Weiss temperature θ was neglected due to the $T \gg \theta$ for these coal type of radicals.

RESULTS AND DISCUSSION

It has been established that coal contains oxygenated complexes even in as received form. During the thermal treatment (low temperature) the released carbon oxide can be detected spectroscopically.

EPR is sensitive enough to reveal very small variation in the electronic structure. Indeed EPR signals from similar coals like Ba, Na and ShG (coming from nearby locations) can be distinguished by linewidth, lineshape and related temperatures dependences.

For all the samples X-band EPR spectra show one single broad signal at room temperature; however a line shape variation has been observed by changing the temperature in the range 50–200 °C; g -factor, linewidth and radical concentration of the powder coal samples were then determined from the measurement. For Kho coal an asymmetric spectrum was obtained at all temperatures (for this sample the EPR parameters were determined in [6] at room temperature). A significant difference in EPR parameters was instead notified in the spectra of TT and KhT coals.

The most coals (TT, KhT, Kho and Ba) show Curie type temperature dependence of the signal intensity, so that paramagnetic centers were localized due to breaking bonds like C–O, C–H and C–C (fig. 1). This increase of the intensity was evident for KhT coal. On the contrary, for ShG and Na coals the signal intensity was weakly depended on the used low temperatures.

From elemental analysis TT sample coal displays an higher carbon content and is thus the only with high rank of bituminous while all the others samples are low carbon content coals that means low rank or brown coals. It was noticed that KhT coal behaves like TT coal. Its radical concentration increased significantly with respect to TT in the 100–200 °C temperature range.

Kho coal shows similar features at 150 °C, however this coal's specific radicals were maintained during the temperature treatment. An almost linear increase of radical concentration has been observed for Ba coal. For ShG and Na coals the highest unstability of unpaired electrons has been observed as results from the hopping values of their radical con-

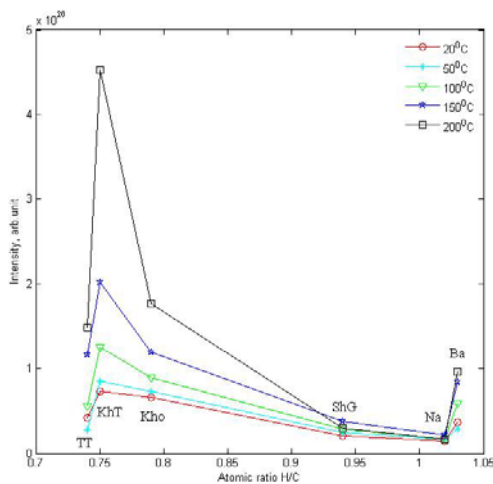


Figure 1. – Effect of used low temperature range on the radical concentration determined as formula (1) and atomic ratio H/C for the studied coals

2,0042 and 2,0041 in the used temperature range. ShG shows the highest value of the g -factor at room temperature among studied coals, though it has dropped abruptly due to the first temperature used, then kept almost constantly.

The g -factor values of KhT and Kho coals are lower (2,0038 and 2,0037) and slightly decrease (up to 2,0033 and 2,0034) with the temperature increase.

An increase of the g -factor was detected only for TT coal (from 2,0034 at room temperature to 2,0036 at 150 °C). This increase of the g -factor can be attributed to the conversion of the material itself. As the result its linewidth also decreases with the temperature.

According to the plot (fig 2) the relation of the g -factor and the free radical concentration is not direct but inverse, lower radicals higher g -factor. Therefore, the lowest radical concentration detected but the highest g -factor are observed for Na sample and then it goes like ShG, Ba and TT. Kho and KhT coals display a smooth decrease in the dependence between the g -factor and the temperature or the radical concentration and the temperature.

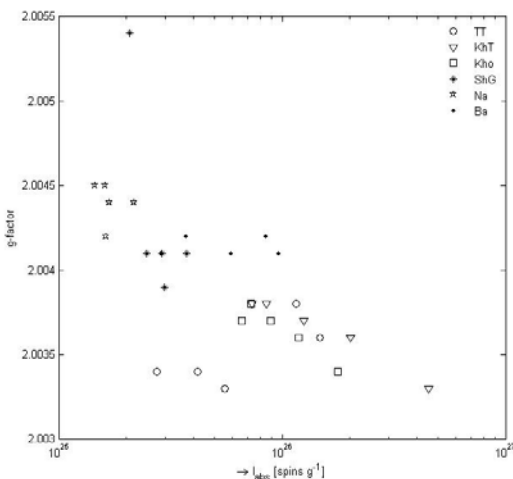


Figure 2. – Plot of the g -factor vs used temperatures for the studied coals

centration suggesting that these radicals may undergo coupling reactions before volatile being condensed.

It is difficult to find a clear and simple dependence in the behaviour of the g -factor at variance with the temperature, but it should be noted here that it tends to decrease with increasing the temperature. Because of the inhomogeneity of coal itself it is estimated an error on the g -factor value of approximately 2×10^{-4} . The g -factor is evaluated as higher value when more unpaired electrons are located in the heteroatoms like O, S and N in coals. The g -factor of brown type coals (Na and Ba) are 2,0045 and 2,0042 at room temperature and has no significant change with slightly decreasing down to

2,0042 and 2,0041 in the used temperature range. ShG shows the highest value of the g -factor at room temperature among studied coals, though it has dropped abruptly due to the first temperature used, then kept almost constantly.

Linewidths of the EPR spectra of the studied coals, affected by the interaction of radical and its environment, were a bit above and below 0,7 mT for brown coals like Ba (0,59 mT), Na (0,76 mT), ShG (0,75 mT). Narrower lines are observed for TT and Kho (0,44 mT)

and KhT (0,33 mT). The temperature increase causes a narrowing of linewidths for TT, KhT and Kho coals while minor or absent effects were observed for Na and ShG. The linewidth of Ba coals slightly increases with a rise of the temperature. A slow increase of Ba coal linewidth is strictly related to the radical concentration curve, thereof an interaction of the electrons is strengthened by a formation of radicals caused by the temperature. A similar conclusion also can be made for ShG and Na coals dependence curves. For TT, KhT and Kho coals a continuous decrease of the linewidth is connected to their chemical structural changes with temperature. Particularly, the appearance of a narrow line in the center of the spectrum was to changes in the composition of the coals due to oxygen and coal interaction; consequently, we think that the narrow line is from fusinite part and the broad line from vitrinite part.

Lineshape has been significantly changed depending on the used temperature range for TT and KhT coals. EPR spectrum of KhT at room temperature (symmetric, low intense and with the g -factor of 2,0038) has been turned into the asymmetric, intense with the g -factor of 2,0033 at 200 °C.

CONCLUSIONS

EPR spectra of coals treated at low temperature were obtained to study the characterization of spontaneous combustion of coal.

During the heat treatment the formation of intermediate radicals has been revealed, whose concentration follows Curie law for TT, KhT, Kho and Ba coals. But in Na and ShG coals the radical concentration remained almost unchanged. The g -factor tends to decrease for all the considered coals (KhT, Kho, ShG, Na and Ba) excluding high rank coal of TT and linewidths generally decrease. TT and KhT coals line shape change significantly due to the temperature.

Acknowledgement. This work was supported by the CICOPS-2016 fellowship program, University of Pavia, Italy and the project #P2016-1216 from the Asian Research Center in Mongolia.

REFERENCES

1. Walter Fuchs, A. G. Sandhoff. Theory of coal pyrolysis. Industrial and engineering chemistry. 1942, 34, p. 567–571.
2. W. B. Davies, D. J. Brown. Mechanism of coal decomposition. Brown Nature. 1967, p. 64–65.
3. L. Petrakis, D. W. Grandy. Formation and behaviour of coal free radicals in pyrolysis and liquefaction conditions. Nature. 1981, 289, p. 476-477.
4. Soon Sam Kim, Mark L. Jarand, Kandaswamy Durai-Swamy. E.s.r. study of pyrolysis vapour of coal. Fuel. 1982, 61 (11), p. 1124-1126.
5. Richard F. Sprecher, Herbert L. Retcofsky. Observation of transient free radicals during coal pyrolysis. Fuel. 1983, 62(4), p. 473-476.
6. S. Munkhtsetseg, N. M. Lapchuk, N. A. Poklonski, N. I. Gorbachuk, Kh. Tsookhuu, G. Shilagardi, N. Tsogbadrakh, A. N. Oleshkevich. (2014): CW EPR study of natural Mongolian coals. 6th International Conference «Materials and Structures of Modern Electronics»' October 8 - 9, 2014, Minsk (Belarus), p. 15–19.