Coal structure in the oxidation

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In the current paper we present the experimental results of Nuurstkhotgor coals in the original (as received) and with low temperature treatment and compared those experimental with the theoretical ones for the observing coal molecule structure specifics in the oxidation. Three groups of the paramagnetic centres are responsible for one narrow Lorentz 1 (0.18 mT), three broad Gaussian 1 and 2 (0.30-0.62 mT), three broadest Gaussian 3 and 4 (0.85-1.05 mT) lines found in the EPR spectrums in the two coal samples.

An infrared spectrum obtained experimentally from the heated coal has established several differences from the spectra of the original coal by its number of the bands and the intensities. Main differences are located in the 3000 and 1000 cm^{-1} absorption region where the vibrations from the O-H and C-O bonding.

I. INTRODUCTION

Coals actively absorb oxygen even in the low temperature [1-3] and relatively active to the oxidation in the air are inclined to the spontaneous combustion. In the interaction of coal with oxygen the influence is more observed in the structural part of petrographic and mineral compound [1], so that the structural properties of coal have been receiving much attention among coal chemists because of their importance in chemical reactivity during various utilizations. Major minerals and quartz in coals are comfortably revealed by the IR and Raman methods, in the same time the correlation method of EPR spectroscopy is used for the determination of the paramagnetic center containment in coal which is proportional to the absorbed oxygen atom number in the oxidation process. In the current paper we present the experimental results of Nuurstkhotgor coals in the original (as received) and with low temperature treatment and compare those experimental results with the theoretical ones for the observing coal molecule structure specifics in the oxidation.

II. EXPERIMENTAL

Samples

Studied coal samples were as following: original coal sample from Nuurstkhotgor deposit and heated one (heating temperature was near 100 °C) in solid state.

Electron Paramagnetic Resonance

The EPR spectra were obtained in the solid state at room temperature (300 K) in quartz tubes. A Radio PAN SE/X 2543 spectrometer was used operating at a frequency of 9.3 GHz (X-band), with a 100 KHz modulation frequency, 0.1 mT modulation amplitude and ≤ 70 mW microwave power. There was used crystal ruby Al_2O_3:Cr, which was fixed on the wall of rectangular shape H_{102} cavity, as an adjustment of phase modulation of magnetic field and calibration of H_1-component of ultrahigh frequency radiation. Ultrahigh frequency field was measured by frequency meter and magnetic field – by the sensor of nuclear magnetic resonance. Modulation amplitude and time constant of EPR registration (10 min) were chosen from well-known requirements for undistorted registration of first derivative resonance absorption signal by magnetic induction [4]. Registered EPR spectrums as a first derivative resonance absorption signal of microwave radiation of studied coals in the magnetic field.

The values of the root-mean-square deviations for the approximations of the experimental spectra by different superpositions of Gauss and Lorentz lines were determined. Those approximations, which gave the smallest RMS deviation, were assumed as the best results of curve fitting [4]:

Gaussian line

$$Y^{'} = -Y_{max}[2(\ln 2)(B - B_{\Gamma} / \Gamma^2) \cdot$$
$$\exp[(-\ln 2)(B - B_{\Gamma})^2 / \Gamma^2]$$

Lorentzian line

$$Y^{'} = -Y_{max}[2\Gamma^2(B - B_{\Gamma})]/[\Gamma^2 + (B - B_{\Gamma})^2]^2$$

where Y_{max} is the maximal absorption amplitude, B and B_r the magnetic induction and the resonance

magnetic induction, and Γ is the halfwidth (linewidths: $\Delta B_{pp} = (2/\ln 2)^{1/2} \, \Gamma$ for Gauss line and $\Delta B_{pp} = (2/3)^{1/2} \, \Gamma$ for Lorentz line).

As the best results of resonance curve fitting those approximations which gave the smallest value of the root-mean-square deviation were accepted.

The parameters of the component lines of the best-fit EPR spectra: g-factor, linewidth (ΔB_{pp}) and integral intensity were evaluated. g-Factor was determined as

$g = h\nu / \beta B_r$

where h is the Planck constant, β the Bohr magneton, ν the microwave frequency, and B_r is the resonance magnetic induction.

IR spectroscopy

Samples for FTIR were prepared using the potassium bromide (KBr) pellet technique. A very small amount of each coal sample (approximately 1 mg) was mixed with 300 mg of KBr to produce the pellets. Fourier transform infrared (FTIR) spectra of pellets samples were recorded on a Perkin Elmer Spectrum BXII FT-IR spectrometer on a spectral range of 4000 to 600 cm^{-1}, employing a resolution of 8 cm^{-1}.

III.   RESULTS AND DISCUSSION

EPR spectra

EPR spectrums both experimental and theoretical of the coals are shown on the figures 1, 2 and 3. Registered a singlet, isotropic EPR signal with g-factor 2.0032 and line width $\Delta B_{pp} = 0.32$ mT for the original Nuurstkhotgor coal (sample *1*). For the heated Nuurstkhotgor coal (sample *2*) the EPR spectrum with g-factor of 2.0032 consists from the seven component lines, placed relatively symmetrical to signal 2.0032. g-factors following first and second spectrums (see. Fig. 1 indicated signals) are: *1* — 2.1545; *2* — 2.0943 at low and high magnetic field value respectively. Third and fourth lines are overlapped by line 2.0032 and weak by their intensity. Linewidth of these components is increasing at high magnetic field. Linewidths of the first line — $\Delta B_{pp} = 1.05$ mT and the second line — $\Delta B_{pp} = 1.13$ mT are two times less than the fifth ($\Delta B_{pp} = 1.77$ mT) and the sixth ($\Delta B_{pp} = 1.94$ mT) lines.

EPR registration was made several times on the same coal sample. Under multiple registration of EPR and at sample turning by 90^0 (relatively to the direction of external magnetic field induction)

in the resonator considerable changes in g-value and line width are not to be observed. The line shape analysis is made on the central line with g-factor of 2.0032 (Fig. 3).

Lineshape of the studied coals indicated their complex character. The original Nuurstkhotgor coal EPR line is a superposition of purely three gaussian lines with g-factor of 2.0032 and line widths of 0.30 mT (gaussian *1*), 0.62 mT (gaussian *2*) and 1.05 mT (gaussian 3) (Fig. 2) and the heated coal's central line of the EPR lines have mixed lines of gaussian and lorentzian with line widths of $\Delta B_{pp} = 0.30$ mT (gaussian 1), $\Delta B_{pp} = 0.51$ mT (gaussian 2), $\Delta B_{pp} = 1.02$ mT (gaussian 3), $\Delta B_{pp} = 0.85$ mT (gaussian 4) and $\Delta B_{pp} = 0.18$ mT (lorentzian 1) (Fig. 3). The best fit of the recorded data (theoretical line) was obtained for approximation of the each experimental spectrum by the sum of the each lorentzian or gaussian lines.

Three groups of the paramagnetic centres are responsible for one narrow Lorentz 1 (0.18 mT), three broad Gaussian 1 and 2 (0.30-0.62 mT), three broadest Gaussian 3 and 4 (0.85-1.05 mT) lines found in the EPR spectrums in the two coal samples.

g-factors are the same to all gaussian and lorentzian lines 2.0032 from the "tore" sp^n bonds (where n=1, 2, 3) in the aromatic and aliphatic structures [1, 5]. The highest g-factor may be indicate the existence of nitrogen, oxygen or sulphur free radicals in the simplest aromatic structures in the analyzed coals.

Infrared spectra

The experimental and calculated infrared spectra of the studied coals are shown in Figure 4. As shown from the infrared spectrums in the long-wave (1500–600 cm^{-1}) and short-wave (4000–3000 cm^{-1}) frequency zones of the heated Nuurstkhotgor coal, an appearance of new bands and an intensification increasing are detected after heated and calculated coal. The absorption band assignments were made in table 1. Below are analyzed the most important bands of IR spectra in details.

Characteristic absorption bands for the heated coal, uppermost, revealed in the short-wave spectral area (4000-3000 cm^{-1}), the peaks 3624 and 3500 cm^{-1} due to O-H stretching of various groups like phenols and alcohol and in the intensities of the most bands, especially, the bands at 1426, 1166, and 1080 cm^{-1}. We paid special attention to the sharp intense two bands from the valence

vibrations of C-O in phenols, ethers and bridge bonds of C_{ar}-O-C_{ar}, C_{ar}-O-C_{al}, C_{al}-O-C_{al} near 1000 cm^{-1} in the spectra of the heated coal [6, 7]. These bands are very weak intensive in the spectra of the original coal. As we see from the figure 5, the main difference between the original and heated coals is in its infrared spectra intensity of the bands in the 1000 cm^{-1} region.

Intensity increase is observed also in the region of the 900–625 cm^{-1} in the infrared spectra of the heated coal, where the three bands at 865, 799 and 778 cm^{-1} from sp^2- (or sp^3-) hybrid bonded aromatic CH-groups.

IV. CONCLUSION

Three groups of the paramagnetic centres are theoretically responsible for one narrow Lorentz 1 (0.18 mT), three broad Gaussian 1 and 2 (0.30-0.62 mT), three broadest Gaussian 3 and 4 (0.85-1.05 mT) lines found in the EPR spectrums in the two coal samples.

An infrared spectrum obtained experimentally from the heated coal has several differences from the spectra of the original coal by its number of the bands and the intensities. Main differences are located in 3000 and 1000 cm^{-1} absorption region where the vibrations from the O-H and C-O bonding.

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Table 1 FTIR band assignments of Nuurstkhotgor coal.

Wave number, cm^{-1}	Assignment	Wave number, cm^{-1}	Assignment
Original coal		Heated coal	
3400 s	ν(O-H)	3624 sh, m	ν(O-H)
			ν(O-H)
3045 m	ν(C-H$_{ar}$)	3500 sh, m	ν(O-H)
			ν(C-H$_{ar}$)
2920 s	ν(C-H$_{al}$)	3404 s	ν(C-H$_{al}$)
2854 sh, s	ν(C-H$_{al}$)	3045 m	ν(C-H$_{al}$)
1796 sh, w	ν(C=O)	2920 s	ν(C=O)
			ν(C=C)
1608 s	ν(C=C)	2852 sh, s	σ(C-H)
1437 s	σ(C-H)	1734 sh, w	ν(C-O)
1370 sh, m	σ(C-H)	1601 s	ν(C-O) or ν(Si-O)
1264 sh, m	ν(C-O-R)	1430 s	σ(C-H$_{ar}$)
			σ(C-H$_{ar}$)
1166 sh, s	ν(C-O)	1166 sh, vs	σ(C-H$_{ar}$)
1081 s	ν(C-O) or ν(Si-O)	1081 vs	σ(Si-O-)
			σ(Si-O-)
865 w	σ(C-H$_{ar}$)	865 m	
799 w	σ(C-H$_{ar}$)	797 s	
778 sh, w	σ(C-H$_{ar}$)	778 sh, s	
754 vw	σ(Si-O-)	738 w	
695 vw	σ(Si-O-)	695 w	

Abbreviations used for relative intensities: [a] vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder.
[b] vibrations having relative intensities less than 0.10 are not reported; Valence vibration symbolized by ν, deformation vibration by — σ