

EPR Characteristics of Activated Carbon for Hydrogen Production by the Thermo-Catalytic Decomposition of Methane

A.B. WIĘCKOWSKI^{a,b,*}, L. NAJDER-KOZDROWSKA^a, P. RECHNIA^c, A. MALAIKA^c,
B. KRZYŻYŃSKA^c AND M. KOZŁOWSKI^c

^aInstitute of Physics, Faculty of Physics and Astronomy, University of Zielona Góra,
Z. Szafrana 4a, 65-516 Zielona Góra, Poland

^bDepartment of Superconductivity and Phase Transitions, Division of Physics of Dielectrics
and Molecular Spectroscopy, Institute of Molecular Physics, Polish Academy of Sciences,
M. Smoluchowskiego 17, 60-179 Poznań, Poland

^cFaculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

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The electron paramagnetic resonance (EPR) method was used to characterize samples of activated coal before and after reactions of the catalytic decomposition of methane and ethanol at temperatures of 1023 K (750 °C), 1123 K (850 °C) and 1223 K (950 °C). The EPR parameters: spectroscopic splitting factor g , peak-to-peak linewidth ΔB_{pp} , and spin concentration c were measured. During the ethanol-assisted catalytic decomposition of methane carbon-located-spin radicals are partially transformed into oxygen-located-spin radicals.

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1. Introduction

The shortcomings of the fossil fuels are their limited availability and emission of greenhouse gases (GHG) such as hydrocarbons and oxides of carbon, nitrogen, and sulfur during the combustion process. This is why since a half of century the attention of researchers is paid to hydrogen, an efficient energy carrier, which is friendly for the ecosystem, because the only product of its combustion or its use in fuel cells is pure water. There are many methods of producing hydrogen, but only two of them are free of the disadvantage of emitting GHG: the water splitting process and the catalytic decomposition of methane (CDM). Methods of water splitting are not economical, but the CDM is characterized by much lower costs. Two kinds of catalysts are used for CDM, namely catalysts containing transition metal elements and carbonaceous catalysts. The former are expensive, undergo deactivation and their regeneration is also expensive, whereas catalysts based e.g. on activated carbon are much cheaper, their activity is admittedly lower, but they are catalytically active for a longer time and their regeneration can be performed by adding ethanol to the gaseous mixture.

The EPR spectroscopy is a very useful technique for studying coals and carbonaceous materials [1]. In the case of coal the source of the EPR signal are unpaired electrons (spins) localized on carbon, nitrogen, oxygen, and/or sulfur atoms.

According to a model given by Kastening [2], the walls of the pores of activated carbon are formed by graphite nanocrystallites containing a small number of graphene layers. It is commonly accepted that the paramagnetic centers in activated carbon are associated with the presence of dangling bonds [3–5]. Because the ratio of surface atoms in activated carbons is high, the excitation of localized charge carriers is easy and high electric conductivity is observed in a wide range of temperatures [6]. The influence of γ -irradiation and activation temperature of activated carbons on the g -value, the linewidth and the EPR line intensity was studied by Erçin et al. [7]. The EPR spectroscopy method was also applied to measure the g -factor, the linewidth and the spin concentration of activated carbons obtained from various plants [8]. In many studies it was found that the g -values of activated carbons are close to the free electron value $g_e = 2.0023$. Some deviations from this value were interpreted by assuming a contribution of the p -orbital of the carbon atom [9]. The changes of the g -factors for different active carbon samples obtained from pecan shells were explained by a probable formation of oxygen-containing functional groups [10]. An EPR analysis of porous carbons allowed to draw the conclusion that on the surface of heterogeneous carbons, three different regions termed activated, graphitized, and highly polar are distributed [11]. The usability of activated carbon in the processes of adsorption and desorption of hydrogen depends not only on the surface area, but also on the origin and chemical character of the carbonaceous material [12].

Activated carbons are used as catalysts in various chemical reactions. One of the applications of these

*corresponding author; e-mail: Andrzej.Wieckowski@vp.p.l

materials is the production of hydrogen by endothermic CDM ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$, $\Delta H_{298\text{K}} = 74.52 \text{ kJ mol}^{-1}$) [13–15]. Ashik et al. [16] pointed to the significance of the process of thermo-catalytic decomposition (TCD) of methane which is performed without disadvantages resulting from the emission of GHG. However, activated carbon undergoes deactivation after some time of its use in the reaction [17, 18]. In this aspect of importance there are studies of the regeneration of deactivated carbonaceous catalyst deposits [16].

By performing the reaction with ethanol on deactivated carbon deposit at different temperatures an effective regeneration of the catalyst can be achieved. Ethanol undergoes decomposition into several compounds, i.e. ethylene ($\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$) which reacts further ($\text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2$) thus restoring the catalytic activity of carbon [17, 18].

2. Experimental

2.1. Preparation of catalyst

Activated carbon for testing the reaction of catalytic decomposition of methane and ethanol was obtained by carbonization of hazelnut shells. The raw material underwent mechanical treatment to obtain particles with the size $\leq 0.5 \text{ mm}$. The chemical activation of the carbon precursor was performed in the presence of potassium hydroxide KOH in nitrogen atmosphere at 1073 K (800 °C) for 45 min. The carbon powder was washed with 5% solution of hydrochloric acid, followed by washing with distilled water and drying overnight at 393 K (120 °C). The physicochemical characteristics of the catalyst samples (proximate and elemental analyses of carbon precursor and activated carbon, and textural properties of selected samples: initial activated carbon, catalysts spent in the reactions of methane decomposition, and catalysts spent in ethanol-assisted methane decomposition carried out at different temperatures) were presented previously [17, 18].

2.2. EPR measurements

EPR spectra for all studied samples were performed with an X-band spectrometer type SE/X (Radiopan, Poznań, Poland) operating at microwave radiation frequency equal to 9.4 GHz and magnetic field modulation frequency of 100 kHz. Before performing the measurements, the activated carbon samples were kept at 333 K (60 °C) for about 12 h in a vacuum $< 10^{-2} \text{ Pa}$. EPR spectra were recorded at room temperature as the first derivative of energy absorption. Linewidth ΔB_{pp} of EPR line is defined as the distance between peak to peak of the first derivative. The applied microwave power was 0.7 mW. The spectroscopic splitting factor g was calculated from the condition of EPR

$$g = (h/\beta)\nu/B_r,$$

where g — spectroscopic splitting factor, h — the Planck constant ($h = 6.62606957(29) \times 10^{-34} \text{ J s}$), β — the Bohr

magneton ($\beta = 9.27400968(20) \times 10^{-24} \text{ J T}^{-1}$), h/β — constant ($h/\beta = 71.4477319(16) \text{ mT GHz}^{-1}$), ν — microwave frequency [GHz], B_r — resonance magnetic field [mT]. A weighed ultramarine sample with the concentration of $c = (2.0 \pm 0.3) \times 10^{20} \text{ spin g}^{-1}$ was used as standard of the number of spins. The spin concentration c_{sample} was calculated with the formula

$$c_{\text{sample}} = c_{\text{ultramarine}}[I/(Gm)]_{\text{sample}}/[I/(Gm)]_{\text{ultramarine}},$$

where c — concentration of spins [spin g^{-1}] of sample and ultramarine, respectively, I — intensity of the line (integral of the absorption), G — receiver gain, m — mass of sample and ultramarine, respectively.

3. Results and discussion

The reaction of methane decomposition was conducted at three temperatures namely at 1023 K (750 °C), 1123 K (850 °C) and 1223 K (950 °C). At the latter temperature the conversion of methane was the highest and equal to 26%. With increase of temperature the equilibrium of the decomposition reaction was shifted towards the production of hydrogen. After some time the pores of the catalyst were blocked by the carbonaceous deposit and the methane conversion decreased.

In the next step the decomposition of methane was performed in the presence of ethanol which during the decomposition process produces ethylene followed by the formation of a carbonaceous deposit capable of restoring the activity of the carbon catalyst. The catalytic reactions of decomposition of methane and of ethanol were carried out in two ways. The former consisted in performing the decomposition of methane and ethanol at the same temperature, while the latter in the decomposition of methane and of ethanol at different temperatures.

When the process of decomposition of methane and ethanol was conducted at the same temperature, the best conversion of methane was obtained at 1223 K (950 °C). The post-reaction mixture of gases consisted of hydrogen, methane, carbon monoxide, carbon dioxide, water, ethylene, ethane, acetaldehyde, and ethanol. A prolongation of ethanol dosing had no influence on the methane conversion. The most probable explanation of this fact is the occurrence of graphitization of the methane-originated and the ethanol-originated catalyst at higher temperatures. It is well known that graphite-like materials are characterized by a very low catalytic activity for the CDM compared with that of carbonaceous materials with a poorly ordered structure.

Surprisingly enough, when the CDM was carried out at 1123 K (850 °C) and the ethanol-assisted CDM at 1223 K (950 °C) with alternate dosing of ethanol, the catalytic activity stabilized for a longer time and methane conversion was about 13%. This result was unexpected, because when both processes were run at the same temperature of 1223 K (950 °C) the methane conversion was lower. A more detailed information on the two ways of running of the both processes was given in our earlier papers [17, 18].

A useful tool for investigating changes in the properties of catalysts during the reaction of CDM is EPR spectroscopy. In this work we present an EPR characterization of activated carbon obtained from hazelnut shells. For samples of pristine activated carbon catalyst and as well as that after the reaction with methane and/or ethanol at different temperatures, the g -factor, peak-to-peak linewidth ΔB_{pp} of EPR spectra, and spin concentration c were analyzed.

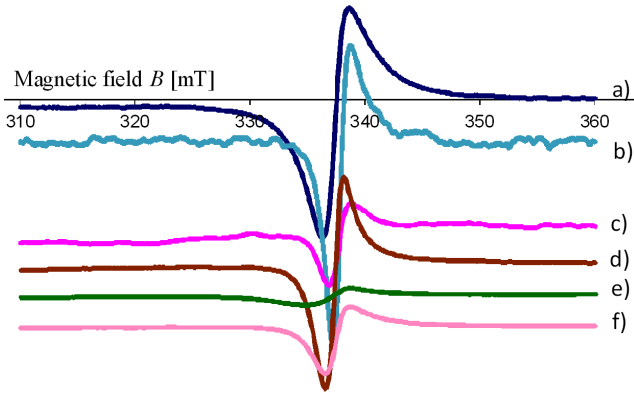


Fig. 1. EPR spectra of selected samples: (a) activated carbon, (b) M-750 °C, (c) M-850 °C, (d) M-750 °C, E-750 °C (60 min), (e) M-850 °C, E-750 °C (60 min), (f) M-850 °C, E-950 °C (60 min). M stands for methane decomposition, E stands for ethanol decomposition, (60 min) — duration of ethanol dosing.

Figure 1 shows the EPR spectra of selected samples. The paramagnetic centers are very sensitive to the influence of oxygen present in air and the EPR spectrum undergoes broadening of the lines caused by the increase of spin–spin interactions. Evacuation of the samples in a vacuum results in a line-narrowing.

It is known that the EPR spectrum of coal is a superposition of a few components of Gaussian shape with wide linewidth and of Lorentzian shape with narrow linewidth [19]. The EPR parameters are sensitive to chemical and thermal treatments and they can give information on the structure of coal. The multi-component character of the EPR spectrum of coal is a result of its complex structure. The values of g -factor are nearly the same for each component and they are related with the value of the spin–orbit coupling constant λ and with the localization of unpaired electrons responsible for the EPR signal [20]. The temperature and the chemical treatments used affect more the linewidth and the concentration of paramagnetic centers [21, 22].

Table I presents the values of the EPR parameters of recorded spectra (g -factor, peak-to-peak linewidth ΔB_{pp} [mT], and spin concentration c [spin g⁻¹]) for selected samples. Following the changes of the g -factor one can observe a decrease of its value for samples used in the reaction of the decomposition of methane (sample M-750 °C, $g = 2.0018$ and sample M-850 °C, $g = 2.0031$)

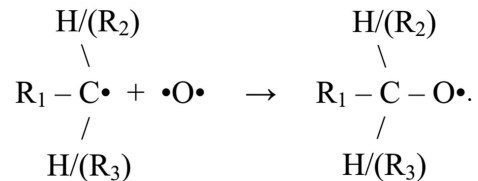
TABLE I

EPR parameters: g -factor, peak-to-peak linewidth ΔB_{pp} [mT], spin concentration c [spin/g] of activated carbon samples.

Sample	g -factor	Linewidth peak-to-peak ΔB_{pp} [mT]	Spin concentration c [spin/g]
activated carbon	2.0037	2.06	55.9×10^{18}
M-750 °C	2.0018	1.54	3.4×10^{18}
M-850 °C	2.0031	1.97	7.8×10^{18}
M-750 °C, E-750 °C (60 min)	2.0043	1.60	21.6×10^{18}
M-850 °C, E-750 °C (60 min)	2.0071	—	—
M-850 °C, E-950 °C (60 min)	2.0027	1.99	11.4×10^{18}

M stands for methane decomposition, E stands for ethanol decomposition, (60 min) — duration of ethanol dosing.

compared to the g -value of the pristine activated carbon ($g = 2.0037$). This suggests that a certain amount of paramagnetic centers existing in the activated carbon in a disordered environment becomes ordered and the g -factor is closer to the free-electron-value $g_e = 2.0023$. For samples which were used in the ethanol-assisted CDM, M-750 °C, E-750 °C, $g = 2.0043$ and M-850 °C, E-750 °C, $g = 2.0071$, the values of the g -factor are distinctly higher. This phenomenon can be explained by the assumption that after the decomposition of the oxygen-containing compound (ethanol) some amount of paramagnetic centers (carbon-located-spin radicals $\text{C}\bullet$) on the surface of the activated carbon are transformed into radicals, where the unpaired electron (spin) is localized on an oxygen-atom $\text{C}-\text{O}\bullet$, according to the schematic reaction



The g -factor is dependent on the kind of atom on which the unpaired electron is localized. As shown by Pryce [20], the g -factor is given by the formula $g_{ij} = g_e(\delta_{ij} - \lambda A_{ij})$, where g_{ij} (in general anisotropic) is a tensor, g_e is the free-electron-value ($g_e = 2.0023\dots$), δ_{ij} is the Dirac delta ($\delta_{ij} = 0$ or 1), λ is the spin–orbit coupling constant for a given atom of a chemical element, A_{ij} is a real symmetrical positive definite tensor defined in terms of the matrix elements of the orbital angular momentum. The tensor indices i, j refer to Cartesian coordinates. The quantity A_{ij} is inversely proportional to the distance of orbital energy levels ($E_n - E_0$), where the indices $0, 1, \dots, n, \dots$ refer to the orbital levels, 0 being the lowest one. The values of the spin–orbit coupling constant λ were calculated by McClure [23],

and some selected values are as follows: for carbon C: $\lambda = -28 \text{ cm}^{-1}$, nitrogen N: $\lambda = -70 \text{ cm}^{-1}$, oxygen O: $\lambda = -152 \text{ cm}^{-1}$, sulfur S: $\lambda = -382 \text{ cm}^{-1}$. This explains why during the transformation of carbon-located-spin radicals into oxygen-located-spin radicals the g -factor is shifted to higher values.

An exceptional case is the decreased value of the g -factor for the sample M-850 °C, E-950 °C, $g = 2.0027$. Probably some oxygen-located-spin radicals undergo decomposition (dissociation) at 1223 K (950 °C) into carbon-located-spin radicals again, and the g -value becomes lower.

The EPR linewidth is a measure of interactions between the paramagnetic centers (magnetic dipoles) themselves (spin-spin interactions) and between the paramagnetic centers and the crystalline solid state structure (spin-lattice interactions). The greatest EPR linewidth was observed for the initial active carbon sample ($\Delta B_{pp} = 2.06 \text{ mT}$). After its use in the reaction of the decomposition of methane at 1023 K (750 °C), the EPR linewidth of the catalysts decreases (M-750 °C, $\Delta B_{pp} = 1.54 \text{ mT}$ and M-750 °C, E-750 °C, $\Delta B_{pp} = 1.60 \text{ mT}$). The catalyst after CDM at 1023 K (750 °C) is characterized by the smallest EPR linewidth. After performing the reaction of methane decomposition at 1123 K (850 °C), the linewidth of the catalysts increases again (M-850 °C, $\Delta B_{pp} = 1.97 \text{ mT}$ and M-850 °C, E-950 °C, $\Delta B_{pp} = 1.99 \text{ mT}$). At both temperatures, 1023 K (750 °C) and 1123 K (850 °C), the linewidths for the ethanol-assisted CDM in the alternate mode of ethanol dosing are slightly higher in comparison with the values obtained after the decomposition of methane alone.

The initial activated carbon is also characterized by the highest concentration of paramagnetic centers (spins) ($c = 55.9 \times 10^{18} \text{ spin/g}$). After the CDM alone (i.e. without ethanol) both at 1023 K (750 °C) and 1123 K (850 °C), the spin concentration c in the catalyst decreases (M-750 °C, $c = 3.4 \times 10^{18} \text{ spin/g}$ and M-850 °C, $c = 7.8 \times 10^{18} \text{ spin/g}$), while the ethanol-assisted CDM in the alternate mode of ethanol dosing leads to an increase in the spin concentration c (M-750 °C, E-750 °C, $c = 21.6 \times 10^{18} \text{ spin/g}$ and M-850 °C, E-950 °C, $c = 11.4 \times 10^{18} \text{ spin/g}$).

It should be kept in mind that the catalytic processes take place only on the catalyst surface, while EPR measurements refer to the sample bulk, and the bulk structure can be quite different from that of the surface.

4. Conclusions

The reactions of catalytic decomposition of methane (CDM) and ethanol generate hydrogen. The influence of the catalytic process of CDM on the activated carbon catalyst is visible in changes of its EPR spectra. After ethanol-assisted CDM some amount of carbon-located-spin radicals on the surface of the activated carbon is transformed into oxygen-located-spin radicals.

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