"CO2 methanation on Rh/gamma-Al2O3 catalyst at low temperature: “In situ” supply of hydrogen by Ni/activated carbon catalyst"

Swalus, Colas ; Jacquemin, Marc ; Poleunis, Claude ; Bertrand, Patrick ; Ruiz, Patricio

ABSTRACT

Nowadays, the control of CO2 emissions is still a challenge. A few alternatives exist but nothing concrete seems to be developed. Instead of catching and storing CO2, one possibility would be its transformation into value added molecules as methane. Rhodium catalysts are active in CO2 methanation reaction. But it seems that a competitive adsorption exist between the two reactants: CO2 and hydrogen. In order to surpass this trouble and increase hydrogen adsorption, a known active catalyst in methanation (Rh/γ-Al2O3) was put into contact with a known active catalyst in hydrogen activation (Ni/activated carbon). Catalysts were prepared by the mechanical mixing of the latter two in different proportions. Catalysts were tested in the low temperature methanation reaction using CO2 and H2. Methane is produced in all cases with a 100% of selectivity. A significant synergy appears in the catalytic activity of this mixed catalyst. Production of methane in mixtures is largely higher than the t...

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Available at: http://hdl.handle.net/2078.1/112030
The effect of ethanol on carbon-catalysed decomposition of methane

Paulina Rechnia a, Anna Malaika a, Lidia Najder-Kozdrowska b, Mieczysław Kozłowski a,∗

a Faculty of Chemistry, Adam Mickiewicz University in Poznań, Grunwaldzka 6, 60-780 Poznań, Poland
b Division of Spectroscopy of Functional Materials, Institute of Physics, Faculty of Physics and Astronomy, University of Zielona Góra, Prof. Z. Szafrana 4a, 65-516 Zielona Góra, Poland

1. Introduction

A perspective of fossil fuels depletion and harsh norms restricting emission of harmful compounds into the atmosphere have prompted the search for new and safe for the environment energy sources. One of the most promising conceptions is the use of hydrogen, characterised by high calorific value and pro-ecological character (the only product of hydrogen combustion is pure water) [1].

At present the production of hydrogen on industrial scale is mainly based on the processes of methane steam reforming and partial oxidation of refinery residues [2,3]. However, in these processes significant amounts of carbon oxides are formed as by-products, so alternative solutions have been searched for. One of such alternative suggestions is generation of hydrogen in the catalytic decomposition of methane (CDM). As follows from literature data, a high methane conversion to hydrogen is mostly obtained over the catalysts containing transition metals [4–8]. Unfortunately, these catalysts undergo gradual deactivation as a consequence of formation of a low-active carbonaceous deposit originating from methane decomposition [6]. Because of relatively high price of such catalysts their regeneration is desirable. It has been shown that regeneration of a deactivated catalyst by

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oxygen, carbon dioxide or steam permits restoration of its initial activity [7,9−11]. However, according to Villacampa et al., the used catalyst after regeneration with the use of oxygen is fully active but in a very short time it gets deactivated again [7]. Moreover, the process of regeneration is a source of significant amounts of carbon oxides [10,12].

An alternative to expensive catalysts based on transition metals are those based on activated carbon [12−18]. Although their activity in CDM reaction is lower [19], they show a number of attractive properties such as low price, resistance to potential polluting substances present in the gas directed to the reactor and high thermal resistance [20]. Because of fast deactivation also carbon catalysts are sometimes subjected to regeneration e.g. by steam [20] or carbon dioxide [21,22]. Another solution for maintain high degree of methane to hydrogen conversion in CDM reaction is the in situ formation of a catalytically active carbonaceous deposit. It is practically realised by introduction of some additives to the reaction system. Muradov performed a series of CDM reactions in the presence of different hydrocarbons, e.g. propane, ethylene and acetylene, introduced into the reactor in a continuous or cyclic way [12,23]. The same author reported that the carbonaceous deposit formed from methane decomposition showed low activity in CDM [12]. His another observation was that admixture of methane with propane did not lead to an increase in the methane conversion. It was explained by the fact that the carbon crystallites obtained from the same family of hydrocarbons (alkanes) are likely to have the same size and structure, so to show a similar activity in CDM reaction. A different result was observed when ethylene was introduced in pulses. In this situation the amount of hydrogen produced considerably increased, which was attributed to the good catalytic properties of the carbonaceous deposit formed in decomposition of ethylene [13].

The influence of ethylene addition on CDM process has also been studied by our group [24], but in our experiment ethylene was supplied to the reactor simultaneously with methane, making 10 or 20% of the mixture content. We noted that with increasing amount of ethylene in the reaction mixture, the content of hydrogen in the effluent gases increases. At the highest temperature applied (950 °C) and at a 20% contribution of ethylene in the mixture with methane, the amount of hydrogen produced was practically at the same level throughout the whole process. A similar phenomenon was reported when propylene was used as an admixture in CDM reaction [25].

Unfortunately, such reagents as ethylene or propylene are expensive and therefore in our earlier work ethylene was obtained in situ in the reaction of oxidative coupling of methane and this process was subsequently combined with the CDM in one reactor [26]. In this study an attempt was made to obtain ethylene in situ from ethanol. The supply of ethanol is high (as bioethanol) and it is relatively cheap [27]. It undergoes decomposition on carbon catalysts in low temperatures (starting from about 120 °C) with formation of ethylene, diethyl ether and acetic aldehyde [28−30]. In higher temperatures the decomposition of ethanol is mainly realised over inorganic catalysts (nickel catalyst [31], iron catalyst [27], molybdenum carbide supported on silica or carbon nanotubes [32]). In this process also hydrogen, methane, ethane, acetaldehyde and diethyl ether were formed besides ethylene. No information was found on the use of carbon catalysts in ethanol decomposition in high temperature.

The main aim of the paper was to investigate the influence of ethanol on catalytic decomposition of methane. This influence was studied with the alcohol dosed into the reaction system alternately with methane. The activated carbon obtained from hazelnut shells was applied as a catalyst.

2. Experimental

2.1. Preparation of catalyst

Activated carbon obtained from hazelnut shells was tested in the reaction of methane and ethanol decomposition. At the first stage carbon precursor was subjected to mechanical treatment in order to get particles of the size ≤ 0.5 mm, then to chemical activation with KOH (precursor to activating agent ratio of 1:1). The activation was performed at 800 °C for 45 min in the nitrogen atmosphere. The activated material was washed with a 5% solution of HCl, next with distilled water and then dried overnight at 120 °C.

2.2. Characterisation of carbon catalyst

Textural properties of the catalyst were determined by nitrogen adsorption at −196 °C on a Micromeritics Sorptometer ASAP 2010. The apparent specific surface area (SBET) was found from the linear form of BET isotherm, while the micropore volume (Vmic) and external surface area of the catalyst (SS) were calculated using the t-plot method [33]. The total pore volume (Vtot) was obtained from the N2 amount adsorbed at a relative pressure close to unity. CHNS elemental analysis was made on an Elemental Analyser Vario EL III. The transmission FTIR spectra of selected samples were acquired using a Bruker IFS 66v/S spectrometer by adding 256 scans at 2 cm−1 resolution. Pressed KBr pellets at a sample/KBr ratio of 1:400 were used. XPS measurements were performed on an ESCALAB-210 spectrometer made by VG Scientific (GB), with the use of Al Kα radiation at the Constant Analyzer Energy CAE = 25 eV. The XPS spectra were smoothed and the Shirley background was subtracted. The calibration was carried out to the main C 1 s peak at 284.8 eV. The XPS C 1 s peaks were deconvoluted into individual spectral lines, treated as asymmetric sums of the Gauss−Lorentz functions. The ratio of the Gauss to the Lorentz lines of 20:80% was assumed. The following binding energies and their assignment to particular species was taken, according to literature data: 284.8 eV (C−C, C−H), 286.3 eV (C−O), 287.5 eV (C≡O, O−C≡O), 289.0 eV (O−C≡O) and 291.3 eV (π−π∗ transition) [34−36]. EPR analysis was performed on an S/EX spectrometer made by RADIOFAN, Poland. Prior to measurements the samples were heated at 60 °C for about 12 h at <10−2 Pa and carefully weighted. The EPR spectra were recorded in the form of the first derivative of absorption at room temperature and at microwave power of 0.7 mW. The microwave radiation from X range of 9.4 GHz frequency and magnetic field modulation of 100 kHz were applied.
2.3. **Catalytic measurements**

The process of methane decomposition was performed dosing alternately methane and ethanol to a vertical fixed-bed quartz reactor. The procedure of the reaction was as follows. For the first hour methane was introduced into the reactor at the rate of 10 cm$^3$/min, and at every 5 min the post-reaction mixture was subjected to chromatographic analysis (TCD detector, argon as a carrier gas). Then the methane supply was cut off and after rinsing the reactor with argon (10 cm$^3$/min) ethanol was introduced into the gas stream. Ethanol was dosed into the reactor by a syringe pump at the rate of 1.4 cm$^3$/h for 15, 30 or 60 min. After this time of ethanol decomposition, the reactor was rinsed with argon once again and the cycle of methane/ethanol decomposition was repeated until the total duration of methane decomposition of 4 h was reached. To get the data for comparison, the methane decomposition was also performed without ethanol and in another process alone ethanol was decomposed. In all processes the catalyst was used in the amount of 50 mg and the temperature of the process was either 750, 850 or 950 °C.

3. **Results and discussions**

3.1. **Characterisation of carbon catalyst**

The carbon precursor (hazelnut shells) and the activated carbon from it were subjected to proximate and elemental analysis. The results are presented in Table 1, while Table 2 shows the data on textural properties of the activated carbon. As follows from the data, the content of ash in the precursor and in the activated carbon is low, which is highly favourable as some mineral compounds could catalyse methane decomposition and hence lead to false results. A considerable content of moisture and volatile matter in the precursor was responsible for the low yield of activated carbon (merely 14.5%). The same data have also shown that the process of chemical activation of the initial material by KOH leads to an increase in the carbon content and removal of a considerable amount of oxygen and hydrogen. In the catalyst obtained carbon makes over 90%, S, N and H occur in trace amounts but oxygen is present in a relatively high amount.

The precursor activation by KOH led to obtaining carbon of relatively high apparent specific surface area of almost 1100 m$^2$/g (Table 2). As follows from a small value of $S_{meso}$ parameter (meso- and macropores surface area), the greatest contribution to $S_{BET}$ is brought by micropores. The microporous character of the catalyst structure is also confirmed by the ratio of micropores volume to total pores volume.

3.2. **Catalytic activity of activated carbon**

3.2.1. **Decomposition of pure methane**

The first stage of the study was realisation of the methane alone decomposition. The reaction was conducted at three temperatures of 750, 850 or 950 °C and its results are presented in Fig. 1. At the lowest of the three temperatures, the maximum degree of methane conversion (at the beginning of the process) was low and amounted only to 3.4%. With increasing temperature of the reaction this parameter increased and at 950 °C the conversion of methane was the greatest and equal close to 26%. This dependence is related to the position of the equilibrium constant of the methane decomposition reaction as with increasing temperature it is shifted towards products formation [24].

With increasing time of the process, the methane conversion decreases as a result of pore blocking by the carbonaceous deposit formed [24,37]. This phenomenon takes place at all temperatures applied but deactivation of the catalyst is faster at higher temperatures. For example, at 850 °C the minimum methane conversion is reached after about 70 min, while at 950 °C – already after about 20 min. Bai et al. explain this fact by a rapid deposition of carbon at higher temperatures [37]. Thus, the resultant methane conversion depends both on the reaction temperature, as well as on the degree of catalyst deactivation.

3.2.2. **Decomposition of methane and ethanol at the same temperature**

As indicated by the results of Muradov [12,23] and our earlier studies [24,26] introduction of additional substances into the methane decomposition reaction system (by either pulse or continuous method) can significantly restrict the deactivation of the carbon catalyst used. Therefore, at the next stage of our study methane decomposition was performed in the presence of a compound capable of formation of carbonaceous deposit potentially active in CDM reaction. The choice of ethanol as such an additive followed from the fact that one of the products of its decomposition is ethylene, which has been shown to restrict deactivation of a carbon catalyst [24,26].

According to Table 3, the decomposition of ethanol over the carbon catalyst studied in temperatures 750–950 °C leads to formation of hydrogen, methane, carbon oxide, carbon

<table>
<thead>
<tr>
<th>Table 1 - Proximate and elemental analyses of carbon precursor and activated carbon (wt.%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Precursor</td>
</tr>
<tr>
<td>Activated</td>
</tr>
</tbody>
</table>

$^d$ daf stands for dry ash free, $^d$ stands for dry basis.
dioxide, water and trace amounts of ethane and acetaldehyde, besides ethylene. Particularly important seems to be the presence of water and carbon dioxide as these compounds can gasify the carbonaceous deposit which additionally increases the catalyst activity [20–22].

In this study CDM process was conducted by introducing ethanol alternately with methane into the reaction system. In the first stage of the study, the decompositions of methane and ethanol were carried out at the same temperatures of 750 °C, 850 °C or 950 °C. Fig. 2 presents the results obtained at the lowest temperature of 750 °C (the arrows mark the time at which ethanol was begun to be introduced). For the sake of clarity of the figures, the time of catalyst regeneration by ethanol and the time of purging the reactor with Ar after ethanol pulses are not included in the plot. As follows from the figure, the pulse introduction of ethanol to the system results in a reduction of the catalyst activity in CDM reaction. This effect is particularly pronounced after the first (60 min) and second (120 min) introduction of ethanol. Moreover, the longer the time of ethanol dosing, the greater the carbon catalyst deactivation. The lowest methane conversion noted was just about 0.14% (after a 4-h cycle of methane decomposition (60 min)/ethanol decomposition (60 min)), which made less than 4% of the initial methane conversion.

These results were quite surprising to us as we expected to get an improvement in the catalytic activity of the activated carbon after introduction of ethanol, similarly as observed for methane decomposition in the presence of ethylene [24]. However, it should be emphasised that the decomposition of ethanol over a carbon catalyst is much more complex as besides ethylene also other products are formed. Moreover, according to Table 3 data, the content of ethylene in the products formed from ethanol decomposition is the greatest when the decomposition takes place at 750 °C and decreases with increasing temperature of this process. As ethylene formed in decomposition of ethanol immediately undergoes further partial decomposition, it can be assumed that the higher the content of ethylene in the post-reaction gases, the lower the degree of its decomposition. Thus, the results prove that in the ethanol-assisted decomposition of methane the amount of ethylene undergoing decomposition with generation of the catalytically active carbonaceous deposit is small. Moreover, according to Table 2, in the process of methane alone decomposition, the specific surface area decreases drastically from 1090 m²/g to 71 m²/g. The decomposition of methane at alternate dosing of ethanol leads to an even greater decrease in the specific surface area to 10 m²/g. Therefore, we cannot exclude that the catalytic activity of the sample covered with a low-active deposit coming from methane alone and of a greater surface area will be higher than that of the catalyst covered with a more active deposit coming from ethanol decomposition but

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} [m²/g]</th>
<th>S_{ext} [m²/g]</th>
<th>V_{tot} [cm³/g]</th>
<th>V_{micro} [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>1090</td>
<td>9</td>
<td>0.54</td>
<td>0.51</td>
</tr>
<tr>
<td>M-750 °C</td>
<td>71</td>
<td>6</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>M-850 °C</td>
<td>10</td>
<td>9</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>M-750 °C_E-750 °C (60min)</td>
<td>10</td>
<td>7</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>M-850 °C_E-750 °C (60min)</td>
<td>21</td>
<td>21</td>
<td>0.017</td>
<td>0.00</td>
</tr>
<tr>
<td>M-850 °C_E-950 °C (60min)</td>
<td>10</td>
<td>9</td>
<td>0.04</td>
<td>0.00</td>
</tr>
</tbody>
</table>

M stands for methane decomposition, E stands for ethanol decomposition.

![Fig. 1](image1.png) **Fig. 1** Methane conversion versus time on stream at different temperatures.

![Fig. 2](image2.png) **Fig. 2** Ethanol-assisted decomposition of methane at 750 °C.
characterized by low specific surface area. It seems probable, especially that the ratio of the two surface areas is 1:7.

The effect of ethanol on methane conversion at 850 °C is completely different. The cyclic introduction of ethanol into the reaction system leads to a successive increase in the methane conversion degree (Fig. 3). When ethanol decomposition is run for 15 or 30 min, an increase in the methane conversion is small in relation to that in the reaction without alcohol addition, but when it is run for 1 h, this increase is much greater. Thus, as expected, the addition of ethanol had a favourable influence on the catalytic properties of the activated carbon used. This influence seems to be related to the amount of the catalytically active ethanol-originated carbonaceous deposit (according to Table 3, the degree of ethylene decomposition is in these conditions higher than at 750 °C). Moreover the specific surface area of the catalyst after decomposition of methane is close to that after ethanol-assisted decomposition of methane (Table 2). So, the catalytic activity of the activated carbon studied cannot substantially depend on the changes in the specific surface area, as probably is the case at 750 °C.

The data presented in Table 3 imply that at 950 °C the total ethylene decomposition takes place, which should result in a considerable improvement in the catalytic activity of activated carbon in CDM process after introduction of ethanol. However, according to Fig. 4, this is not the case. After the first dose of ethanol, only a small increase in methane conversion is observed, and introduction of ethanol in the two subsequent doses either do not change or even decreases the catalyst activity. Extension of the time of ethanol dosing has only slight effect on methane conversion and the dosing time increase from 30 to 60 min has practically no effect. These observations are most probably a result of graphitisation of both methane-originated and ethanol-originated deposit taking place at high temperature. It is known from literature that the degree of graphitisation of carbonaceous deposit increases with increasing temperature and time of heating [18,36]. On the other hand, graphite-like materials show much lower catalytic activity in CDM than the carbon materials of a low degree of structural ordering [39], which can explain the above observations.

3.2.3. Decomposition of methane and ethanol at different temperatures

In order to get a better insight into the methane decomposition at the alternate dosing of ethanol, at the next stage of the study the decomposition of methane and ethanol were carried out at different temperatures. As at 750 °C the influence of ethanol on CDM process was negative (Fig. 2), in the following part of investigations the decomposition of methane was performed at 850 or 950 °C. At each of these temperatures the duration of ethanol dosing into the reactor was 60 min, as for such a duration of dosing the influence of ethanol on methane conversion was the greatest (Figs. 3 and 4).

Fig. 5 shows the results of ethanol-assisted CDM at 850 °C. The higher the temperature of ethanol decomposition, the more pronounced the increase in methane conversion is observed, and introduction of ethanol in the two subsequent doses either do not change or even decreases the catalyst activity. Extension of the time of ethanol dosing has only slight effect on methane conversion and the dosing time increase from 30 to 60 min has practically no effect. These observations are most probably a result of graphitisation of both methane-originated and ethanol-originated deposit taking place at high temperature. It is known from literature that the degree of graphitisation of carbonaceous deposit increases with increasing temperature and time of heating [18,36]. On the other hand, graphite-like materials show much lower catalytic activity in CDM than the carbon materials of a low degree of structural ordering [39], which can explain the above observations.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Concentration [mol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>750 °C</td>
<td>14.02</td>
</tr>
<tr>
<td>850 °C</td>
<td>17.53</td>
</tr>
<tr>
<td>950 °C</td>
<td>23.43</td>
</tr>
</tbody>
</table>
conversion. The most pronounced effect on the catalyst activity had the decomposition of ethanol at 950 °C. This observation was rather surprising as when both processes were conducted at 950 °C the introduction of ethanol was only a little effective, which was explained by graphitisation of the carbonaceous deposit (Fig. 4). However, the graphitisation of the methane-originated deposit at 950 °C is greater than at 850 °C [38]. Moreover, the graphitisation degree of the solid carbon obtained from decomposition of ethylene or acetylene is lower than that obtained from methane [38].

This means that for the methane decomposition at 850 °C/ethanol decomposition at 950 °C, the resultant catalytic activity of the methane-originated + ethanol-originated deposits is greater than that obtained when both processes are conducted at 950 °C.

Methane conversion for CDM at 950 °C and at alternate dosing of methane and ethanol are shown in Fig. 6. After the first cycle of methane decomposition (950 °C)/ethanol decomposition (750 °C) the methane conversion increases. The decomposition of alcohol after 120 and 180 min does not result in a further increase in methane conversion (the catalyst activity is stabilised at a certain level) which can be a consequence of small amounts of the ethanol-originated deposit formed (Table 3). The periodical decomposition of ethanol at 850 °C gives a clear and gradual increase in the activated carbon activity. The highest degree of methane conversion obtained in these conditions was 13% (after 180 min). When both processes are run at 950 °C the results are not so good, despite the greatest amount of ethanol-originated deposit formed, which can be related to the above mentioned graphitisation.

3.2.4. FTIR, XPS and EPR measurements of fresh and spent carbon catalysts
In order to get a better insight into a possible reason for changes in conversion of methane in the processes studied, selected samples were subjected to FTIR, XPS and EPR investigations. Results of the FTIR analysis are presented in Fig. 7. Unfortunately, activated carbon as a “black material” is characterised by low transmittance of infrared radiation and that is why the spectra of the catalysts are devoid of details. The majority of the spectra show practically only one band at 1600 cm⁻¹, assigned to the stretching vibrations of aromatic structures or coupled carbonyl groups [39]. The spectra of some samples also show a weak band in the range 1000–1300 cm⁻¹. This band is difficult for interpretation as it appears as a result of overlapping of a few bands (fingerprint region, C–O stretching, bending vibrations of O–H from alcohol, phenol or carboxyl groups) [40,41]. The spectra of the catalysts after decomposition of methane alone and after alternate decomposition of methane and ethanol are very...
Results of EPR and XPS analyses of selected samples collected in Table 4. Analysis of these data shows that after methane alone decomposition at 750 °C the FWHM of graphite peak increases, which means that the carbonaceous deposit formed has a less ordered structure than the initial activated carbon. In spite of this, the catalytic activity of the catalyst decreases, which should be related to the earlier-mentioned drastic decrease in the specific surface area caused by the catalyst pore blocking by the carbonaceous deposit formed. When CDM was run at the alternate dosing of ethanol at 750 °C the carbonaceous deposit formed is a bit more ordered than the initial activated carbon and causes an even greater decrease in the specific surface area. Both processes (increase of carbon structure ordering and drop in the surface area) lead to a decrease in the catalytic activity. A certain increase in the structural ordering and a great decrease in the specific surface area take place after decomposition of methane alone at 850 °C, which also result in low catalytic activity. Introduction of ethanol into the CDM system at 950 °C leads to a further increase in the degree of ordering of the carbonaceous deposit, but in this case it results in a certain enhancement of the catalytic activity (Fig. 5). This observation implies that the specific surface area (pore blocking) and degree of ordering of the carbon catalyst structure are important but only one factors influencing its catalytic activity. For instance, in our earlier work we have suggested that the permeability of carbonaceous deposit layer for methane also affects the catalytic activity of activated carbon [22].

Table 4 presents also results of EPR analysis of selected samples. According to some authors, the width of EPR line is related to the number of structural defects in carbon materials [45]. By far the greatest peak-to-peak line width is found in the spectrum of the initial activated carbon, which suggests the highest concentration of defects (the lowest structural ordering). The initial activated carbon is also characterised by the highest concentration of paramagnetic spins, which can suggest that some types of defects stimulate their appearance. After the decomposition of methane alone both at 750 and 850 °C, the EPR line width of the catalyst decreases, while the ethanol-assisted decomposition of methane in the alternate mode of ethanol dosing leads to an increase in the EPR line width (relative to the values obtained after decomposition of methane alone). The changes in spin concentration show the same pattern. It should be noted that the spectroscopic splitting factor (g-value) of the samples studied is close to the value obtained for graphite which is 2.0031 [46]. Unfortunately, it is difficult to find any correlation of the above relations with the catalytic activity of the samples studied or with the earlier discussed XPS results. The most probable explanation is that the catalytic processes take place only on the

**Fig. 8 — XPS C 1 s spectrum of the initial activated carbon.**

![XPS C 1 s spectrum](image)

**Table 4 — Results of EPR and XPS analyses of selected samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>g-value</th>
<th>Peak-to-peak line width [mT]</th>
<th>Spin concentration [10^18 spin/g]</th>
<th>FWHM of XPS C 1s peak component at 284.8 eV [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>2.0046</td>
<td>2.06</td>
<td>55.9</td>
<td>1.97</td>
</tr>
<tr>
<td>M-750 °C</td>
<td>2.0036</td>
<td>1.54</td>
<td>3.4</td>
<td>2.02</td>
</tr>
<tr>
<td>M-750 °C_E-750 °C (60 min)</td>
<td>2.0052</td>
<td>1.50</td>
<td>21.6</td>
<td>1.96</td>
</tr>
<tr>
<td>M-850 °C</td>
<td>2.0034</td>
<td>1.97</td>
<td>7.8</td>
<td>1.92</td>
</tr>
<tr>
<td>M-850 °C_E-950 °C (60 min)</td>
<td>2.0036</td>
<td>1.99</td>
<td>11.4</td>
<td>1.86</td>
</tr>
</tbody>
</table>
catalyst surface (also XPS analysis brings data on the surface), while EPR measurements refer to the bulk sample, and the bulk structure can be significantly different from that of the surface.

4. Conclusions

In this study the microporous activated carbon obtained from hazelnut shells was tested as a catalyst in the catalytic decomposition of methane (CDM). This catalyst was active in the process but it underwent fast deactivation as a consequence of formation of a low-active carbonaceous deposit on its surface. Modification of the process involving the alternate decomposition of methane and ethanol caused changes in the catalyst activity. One of the products formed as a result of ethanol decomposition was ethylene, whose decomposition led to generation of carbonaceous deposit active in the CDM process. When the two reactions (the decomposition of methane and ethanol) were run in the same temperatures, the highest methane conversion was observed at 850 °C. When the above reactions took place at different temperatures, the most effective was the process with methane decomposition at 850 °C, while ethanol decomposition at 950 °C. The duration of ethanol dosing also affects the catalyst activity, the longer the duration the greater the effect, which is related to the greater amount of carbonaceous deposit formed on the catalyst surface.

Acknowledgements

This work was supported by the Polish Ministry of Science and Higher Education (Grant No. N N204 092435).

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