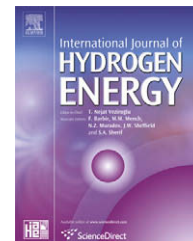


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# Influence of ethylene on carbon-catalysed decomposition of methane

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## ABSTRACT

Catalytic decomposition of methane is a much promising pro-ecological method of hydrogen production. However, the drawback of this method is fast deactivation of the catalyst by deposition of a low-active methane-originated carbon on its surface. In this study an attempt has been made to reduce the process of catalyst deactivation by adding admixture of ethylene to methane directed to the reactor. The study has been performed on the activated carbon obtained by  $\text{Na}_2\text{CO}_3$  activation of pine wood and two commercial types of activated carbons. All the carbon types have been subjected to ultimate analysis, determination of the surface area and pore structure. It has been shown that ethylene also forms a carbonaceous deposit but in contrast to the methane-originated deposit the ethylene-originated one shows good catalytic properties in the reaction of methane decomposition. The addition of 20% ethylene seems to be optimum for ensuring high yield of hydrogen for a long time. The ethylene admixture addition is the more effective the higher the temperature of the process.

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## 1. Introduction

Currently, hydrogen is an important chemical reagent and in future its role is expected to increase because of its use as fuel in cars, fuel cells, etc. Unfortunately, the often-applied industrial method of hydrogen production from natural gas based on steam methane reforming (SMR) [1], is not an ecologically friendly process as it leads to liberation of carbon dioxide – one of gases responsible for the greenhouse effect. For this reason much attention has been paid to the search for more pro-ecological methods of obtaining of hydrogen from methane. One of the methods proposed is the catalytic decomposition of methane [2–9]. This process is not only ecologically friendly but also more economic as it uses much less energy than the classical SMR. The energy requirement for production of 1 mol of hydrogen in the catalytic decomposition of methane amounts to 38 kJ, while it is 63 kJ/mol  $\text{H}_2$

in SMR [10]. The energy needed can be obtained by combustion of about 10% of methane (not recommended as  $\text{CO}_2$  is produced) or by combustion of about 14% of the hydrogen produced (zero  $\text{CO}_2$  emission). Moreover, the carbon obtained in the catalytic methane decomposition (besides hydrogen) can be characterised by a large contribution of nanotubes [11], carbon filaments [12] or carbons showing properties of molecular sieves [13]. These carbon materials can find wide practical use.

Decomposition of methane has been studied for many years. Initial attempts were made without catalysts, however then high pressure and high temperature were needed to ensure a satisfactory reaction rate [14]. Much better results were obtained in the presence of catalysts. Good catalysts of this process were found to be carbon materials and metal-containing systems. Many metallic catalysts, including Co-, Cr-, Ni-, Fe-, Mo-, Pt-, Pd- and Rh-containing ones have been

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tested [10,15]. The metal was usually supported on silica or alumina. Methane decomposition was also performed on binary catalysts containing such systems as Fe/Pd, Fe/Mo and Fe/Ni [10]. The results have proved that the use of a metallic catalyst leads to a significant decrease in the temperature of methane decomposition. For some metallic catalysts traces of hydrogen were detected already at about 473K [15].

Metallic catalysts applied in methane decomposition permit getting gas of initially high content of hydrogen, but their activity decreases very fast with time. This decrease is a consequence of blocking of the active sites of the catalysts by the carbonaceous deposit forming in the reaction [11]. Another problem related to the use of inorganic catalysts is the separation of the catalyst from the carbonaceous deposit. Moreover, the carbonaceous deposit can react with metals to give carbides. Some authors suggest that the carbonaceous deposit should be removed from the catalysts by combustion or gasification by steam [16]. Unfortunately, these processes lead to formation of carbon dioxide and the whole method loses its pro-ecological character. The above problems can be partly avoided by the use of carbon catalysts. The catalysts are highly stable, relatively cheap and resistant to poisoning by sulphur compounds and other elements [11], and undergo deactivation to a much lower degree than metallic catalysts. Unfortunately, the process of removal of the carbonaceous deposit in order to restore the initial activity by combustion in oxygen atmosphere is difficult as along with the deposit also the catalyst is combusted [17]. Muradov has shown that the catalyst can be partly regenerated with the help of unsaturated or aromatic hydrocarbons, but he performed his studies on quartz wool [15] or activated alumina [18]. To the best of our knowledge, no such attempts have been made on activated carbon catalysts. To bridge this gap, our study was undertaken to analyse the influence of unsaturated hydrocarbon (ethylene) on deactivation of the activated carbon catalysts used in the reaction of methane decomposition.

## 2. Experimental

### 2.1. Activated carbons samples

The study was performed on the activated carbon obtained from biomass (pine wood sawdust). The precursor was sieved to the size  $\leq 0.4$  mm, and chemically activated with  $\text{Na}_2\text{CO}_3$  [19]. The activation involved impregnation of the precursor with a 50% water solution of  $\text{Na}_2\text{CO}_3$ , drying of the mixture at 383K, and thermal treatment at 1073K. The weight ratio of  $\text{Na}_2\text{CO}_3$ /precursor was 4:1 and the thermal treatment was performed in a horizontal reactor (heated by tube furnace) for 45 min under argon flow at the rate of  $50 \text{ dm}^3/\text{h}$ . The product was washed with distilled water, 10% HCl and then again with distilled water till the disappearance of chloride ions. The activated carbon was dried at 383K to constant mass. Its yield amounted to 16%. The sample obtained in this way was labelled PAC (pine wood activated carbon).

For comparative reasons two commercially available carbons were also used: RX 3 EKSTRA (NORIT) and WG-12 (GRYFSKAND in Hajnówka, Poland). These samples were labelled RX-3 and WG-12, respectively.

### 2.2. Characterisation of activated carbons

The activated carbons were subjected to ultimate analysis on Elemental Analyser Vario EL III. The porous structure of the samples was determined by a Micromeritics Sorptometer ASAP 2010 with nitrogen as the adsorbate at 77K. The total specific surface areas and pore volumes were calculated using the BET equation, whereas t-plot method was applied to calculate the micropore volume and micropore surface area [20].

### 2.3. Catalytic tests

The catalytic methane decomposition was carried out in a vertical continuous-flow fixed-bed quartz reactor of the inner diameter of 9 mm, at 1023, 1123 or 1223K. The catalyst samples (50 mg) were placed on a layer of quartz wool and a thermocouple (protected by a quartz jacket) was introduced into the catalyst bed to control the temperature of the tube furnace with the reactor. On heating up the tube furnace, argon (99.996% from Messer,  $30 \text{ cm}^3/\text{min}$ ) was blown through the reactor. Having reached a target temperature, argon was replaced by reaction mixture and its flow rate was set at  $10 \text{ cm}^3/\text{min}$ . The experiments were made on pure methane or mixtures of methane–ethylene containing 10–20% of ethylene. The catalytic test lasted for 4 h and the gases released from the reactor were analysed every 15 min. The gas analysis was made by the chromatographic method using a TCD detector and a 3 m column of Porapak Q with argon as the carrier gas.

## 3. Results and discussion

### 3.1. Samples characterisation

All activated carbons investigated were subjected to ultimate analysis and to determination of ash content. As follows from the results (Table 1) the activated carbon PAC has a lower content of ash than WG-12, but higher than RX-3. Most probably the differences are related to the acidic treatment in the process of carbon production. WG-12 most probably was not treated with acid, PAC was washed with diluted HCl (see Section 2), while RX-3 was subjected to a special acidic treatment [21]. Results of the ultimate analysis reveal that all the samples have low contents of sulphur and nitrogen and that the composition of PAC is intermediate between that of WG-12 and RX-3.

**Table 1 – Ultimate analyses of activated carbons investigated (wt %, dry basis).**

Sample	Ash	C	H	N	S	O <sup>a</sup>
PAC	5.8	86.2	0.8	0.3	0.2	6.7
WG-12	11.2	78.5	1.2	0.4	0.4	8.3
RX-3	2.1	92.1	0.5	0.4	0.4	4.5

a Calculated by difference.

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