# CATALYTIC DIRECT DECOMPOSITION OF NATURAL GAS AND LPG FOR PURE HYDROGEN PRODUCTION

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*On γ-$Al_2O_3$ supports, the catalysts containing VI group (Cr and/or Mo) and/or VIII group (Ni and/or Co) metals were prepared. These catalysts were tested in decomposition of natural gas and LPG (Liquefied Petroleum Gas) at temperature ranging between 500-700 $^o$C. Hydrogen concentration is at the maximum level in catalysts containing VIII group metals (Ni and Co) and lower in catalysts containing VI group metals (Cr or Mo). At the decomposition of natural gas, catalyst containing Ni and Co on γ-$Al_2O_3$ support under the same conditions is more active than on $SiO_2$. The influence of the oxidative coke regeneration number on the most active catalyst was studied. Oxidation character and amount of coke which was formed on the catalysts in reaction conditions were studied by means of DTG (Differential Thermo Gravimetric) method.*
***Keywords**: Direct decomposition, Natural gas, LPG(Liquid Petrol Gas), Catalyst, Coke formation, Oxidative regeneration.*

## 1. Introduction

Application of hydrogen as a clean energy source in various fuel cells is one of the most important problems that our world is facing today. For this reason, the development of new, advanced and effective catalysts and the process for hydrogen production are very important. More than 90% of hydrogen production in the world is made by means of reforming hydrocarbon feed stock (natural gas, coal etc.). There are different catalytic methods for the production of hydrogen from methane [1-19] which may be divided into three groups in reforming methane by water steam, partial oxidation and direct decomposition.

Methane steam reforming is generally realized on the catalysts containing Ni, Co or other metals on different supports such as oxides and zeolites at 700-800 $^o$C and under atmospheric pressure [1-5]. Main advances of these processes are the total formations of 4 moles $H_2$ from 1 mole of $CH_4$:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad (1)$$
$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2)$$
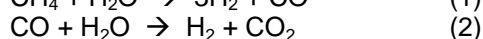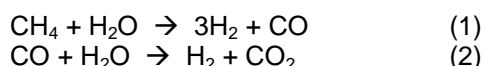
Process of partial oxidation of methane at the different reaction conditions and the type of catalysts has also widely been studied [6-10]:

$$CH_4 + 1/2\,O_2 \rightarrow 2H_2 + CO \qquad (3)$$
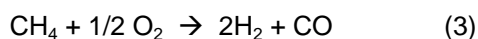
Formation of CO and/or $CO_2$ gases and conducting processes at high temperature are main disadvantages of steam reforming and partial oxidation processes of methane. For this reason, low temperature decomposition of methane is more important, which is formed of $CO_x$-free hydrogen and allows for direct application of it in PEM fuel cells. In spite of coke formation on catalyst surface in this process, simplicity of the direct decomposition processes of methane makes it advantageous in technological terms.

Recently, besides steam reforming and partial oxidation processes of methane, many researches deal with the direct decomposition process [11-29]:

$$CH_4 \rightarrow 2H_2 + C \qquad (4)$$
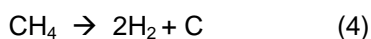
Generally, selection of more active and selective catalysts and realization of direct decomposition processes of methane at lower temperatures are the subject matter of these investigations. Mainly, the catalysts for the decomposition processes of methane are

containing Ni and Fe metals on the $Al_2O_3$ and $SiO_2$ supports with porosity and high surface area.

Chen et al. have studied the direct decomposition process of methane on Ni-Cu-alumina catalyst at temperature ranging between 500-800 $^oC$ [11]. It has been observed that with the rise in temperature, the conversion of methane increased and the stability of catalyst decreased. The effect of Cu to stability of catalyst was established.

Ermakova et al. have studied [12] the behavior of Ni-$SiO_2$ and Fe-$SiO_2$ catalysts under direct decomposition condition of methane, which was prepared by hetero phase sol-gel method. More particularly, formation of silicates between Fe, Ni and $SiO_2$ and its influence on the amount of coke were studied. Formation of silicates in the Ni containing catalysts is strongly affected by the decrease of coke amount while the same effect was insignificant in the case of Fe containing catalysts. Almeida et al. [13] have observed that in direct decomposition processes of methane, on the surface of Ni–doped $Al_2O_3$ spherical catalysts, single-walled and multi walled nanotubes containing coke are formed. Mimura et al. have showed that H-beta and H-ZSM-5 types zeolite supports are effective for Ni catalysis in direct decomposition of methane [14].

Venugopal et al. have studied the decomposition of methane into hydrogen and carbon on Ni/$SiO_2$ catalyst using 5- 90 wt % Ni loading. Among all Ni loadings, 30 wt % Ni on silica has shown good activity and longevity at $600^0C$ [15]. Mohammad S. Rahman et al. [16] have studied methane cracking on a 5 wt % Ni / γ-$Al_2O_3$. The results showed that faster rates of carbon deposition were obtained at temperature 600-$650^0C$.

Echegoyen et al. has confirmed that the presence of copper enhances hydrogen production and the best results were obtained for Ni-Cu-Mg catalysts prepared by the fusion method, reaching a hydrogen production of 80 vol.% [17]. Echegoyen et al. [18] has also studied the effect of catalyst calcinations temperature on hydrogen yields and characteristics of obtained carbon.

Thermo-catalytic decomposition of methane over different carbonaceous materials has been studied by means of using a thermo-balance by monitoring the mass gain (the amount of carbon deposited) with time [19]. The catalytic decomposition of $CH_4$ for the production of pure $H_2$ is carried out over Ni supported on hydroxyapatite [$Ca_5(PO_4)_3(OH)$] catalysts at $650^0C$ and atmospheric pressure. It is found that 30 wt. % Ni/Hap displayed higher hydrogen production. CH4 decomposition activity is decreased with time on stream and is finally deactivated completely [20].

Moliner et al. [21] have studied the thermo-catalytic decomposition of methane using NiMg and NiCuMg catalysts. In all cases, NiCuMg catalyst showed a high and almost constant hydrogen yield without any signs of catalyst deactivation after 8 hr on-stream.

Recently, the researches have focused on developing more active catalysts in low temperature for direct decomposition of methane [22-27]. The methane decomposition process was realized on Ni/$CeO_2$ catalyst at 500 $^oC$ [22]. In this process, besides $H_2$, relatively high amounts of CO were formed. These results were explained as the formation of solid solution of Ni-O-Ce during direct decomposition process. Ni supporter catalyst [23] and the novel nickel oxide catalyst with controlled crystalline size and fibrous shape [24] are used for the low temperature decomposition of methane. Couttenye et al. [25] and Wang et al. [26] at 500-550 $^oC$ have realized the direct decomposition of methane accordingly on Ni +NiO and $Ni_xMg_yO$ catalysts. Ashok et al. has studied hydrogen production by catalytic decomposition of methane over Ni on HY, USY, $SiO_2$ and SBA-15 supports at $550^0C$ and atmospheric pressure. The catalytic activities and the life times of the catalysts are evaluated and discussed. Among the catalysts tested, Ni supported on HY zeolite showed a higher activity [27].

Suelves et al. have showed that the decarbonization of natural gas by thermo-catalytic decomposition (TCD) to produce hydrogen and carbon is a very attractive alternative method to steam methane reforming (SMR). Carbon blacks with high surface area provide relatively high methane decomposition rate [28]. The effect of catalyst preparation methodology on the activity of the iron-based catalyst is studied by Konieczny et al. [29]. The catalyst was synthesized from magnetite by the reduction in the presence of a reducing gas (hydrogen or methane) using a fixed-bed flow reactor. Reduction under methane was found to synthesize a catalyst with the desired properties and smallest preparation time.

Analysis of literature has shown that although the direct decomposition process of methane for $H_2$ production was widely studied, the production process of $H_2$ from practically important commercial gases as natural gas and specially LPG (Liquefied Petroleum Gas) was investigated far less sufficiently. Therefore, the aim of the present research is to investigate $H_2$ production processes from natural gas and LPG by catalytic decomposition. For this matter, the different catalysts containing VI and/or VIII metals were prepared mainly on γ-$Al_2O_3$ support and the activity of these catalysts in different temperature and regeneration of them with air and their stability were investigated. By means of using DTG (Differential Thermo Gravimetric) method, the amount and the character of formed coke were studied.

## 2. Experimental

The catalysts that were prepared on the supports ($\gamma$-$Al_2O_3$ or $SiO_2$) by adsorption of water solutions of $Ni(NO_3)_2 \cdot 6H_2O$; $Co(NO_3) \cdot 6H_2O$; $CrO_3$ and $(NH_4)_2MoO_4$. $\gamma$-$Al_2O_3$ (3mm cylindrical pellets) were taken from Saint-Gobain Nor Pro Corporation (USA) ; micro porous $SiO_2$ (spherical form ø3-5mm) and industrial Al-Ni-Mo catalyst was obtained from Gorky Catalyst Factory (Russian Federation). The catalysts were dried at 150 $^o$C and were calcinated in stages at 450-750 $^o$C in air medium. The amount of active metal (or metals) in catalysts was 10-30 mass %.

The decomposition processes of natural gas and LPG were carried out in a quartz-tube fixed bed flow reactor ( 22mm inner diameter) heated by an electric furnace. 5 or 2.5 grams of catalyst samples were used for experimentation. The temperature in reactor was controlled by means of PID controller systems. The compositions of natural gas, LPG and reaction products were analyzed by Agilent Technology 6890N Network GC System. Generally, the catalysts were studied in atmospheric pressure, 500-700 $^o$C temperature range and 1500 hour$^{-1}$ gas space velocity. The amount and character of formed catalysts cokes were studied by means of using DTG method with a Shimadzu TA-60.

The composition of natural gas and LPG which are used in the present study as raw materials is specified in Table 1.

**Table 1.** The composition of natural gas and LPG (mol, %)

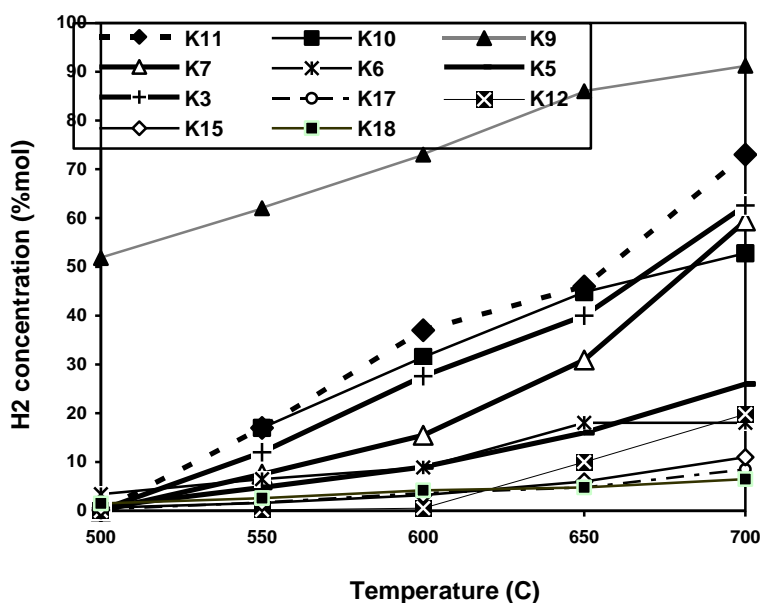|  | Natural Gas | LPG |
|---|---|---|
| $H_2$ | 0.14 | 0.20 |
| $CH_4$ | 87.77 | 0.60 |
| $C_2H_6$ | 4.16 | 15.98 |
| $C_3H_8$ | 0.89 | 50.52 |
| $C_3H_6$(propen) + $C_3H_4$ (allen) | 0.30 | 0.44 |
| $C_4$ (saturated) | - | 29.04 |
| $C_4$ (unsaturated) | - | 0.11 |
| $C_5$ | 0.03 | 0.19 |
| $N_2$ | 5.60 | 1.78 |
| $O_2$ | 0.51 | 1.11 |
| CO | - | - |
| $CO_2$ | 0.43 | - |
| $\Sigma$ S | 0.07 | 0.03 |

## 3. Results and Discussion

For the direct decomposition of natural gas and LPG the catalysts below has been prepared and observed:
%10Ni / $\gamma$-$Al_2O_3$ (K-3); %10Ni+%10Cr / $\gamma$-$Al_2O_3$ (K-5); %10Ni+%10Cr+%10Mo/$\gamma$-$Al_2O_3$ (K-6); %10Co/ $\gamma$-$Al_2O_3$ (K-7); %10Ni+%10Co / $\gamma$-$Al_2O_3$ (K-9); %20Ni/$\gamma$-$Al_2O_3$ (K-10); %10Ni+%10Co / $SiO_2$ (K-11); %10Co+%10Mo / $\gamma$-$Al_2O_3$ (K-15); %10Cr / $\gamma$-$Al_2O_3$ (K-17) and % 10 Mo/ $\gamma$-$Al_2O_3$ (K- 18). For the comparison, the industrial Al-Ni-Mo catalyst (K-12) was also studied.

The catalysts were not specially activated with hydrogen before the usage. Therefore, it has been observed that not depending on the temperature of the reaction there has been an induction period on all the catalysts. The duration of the relevant period could differ between 20 and 45 minutes according to the catalysts type and reaction temperature and the efficiency of the catalysts compared to the hydrogen is rather low. Besides, it has also been observed that the relevant period is shortened with the increase of the temperature. On the other hand, it has also been observed that carbon dioxide and water was formed as a result of the reduction of the metal oxides on the surface of the catalysts during the induction period. The actives that the catalysts showed during the direct decomposition reaction of methane were evaluated after the induction period was over.

The results of $H_2$ formation on different catalysts by decomposition of natural gas are presented in fig.1. As shown in the relevant table, for all catalysts at temperature 500 $^o$C, the concentration of hydrogen is low. When the temperature is increased from 500 $^o$C to 700 $^o$C, independent from the type of catalysts, concentration of hydrogen increased.
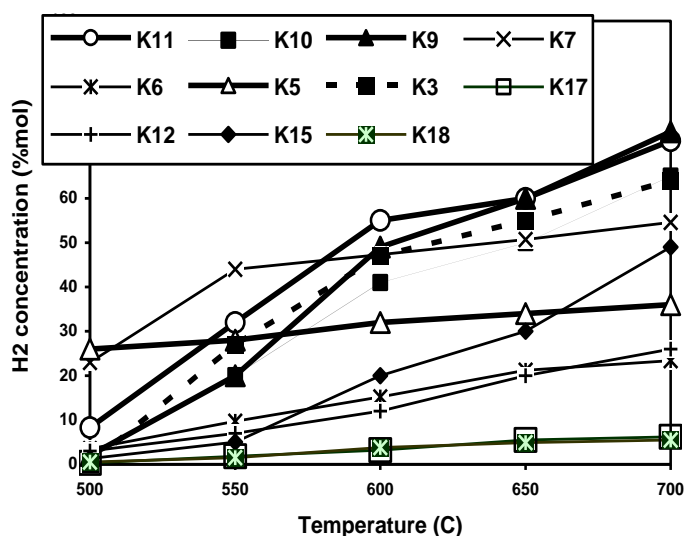
**Fig.1**. Influence of catalyst type and reaction tempe- rature on the $H_2$ formation from direct decomposition of natural gas ( Where: K-3,K-7,K-9,K-10 and K-11 catalysts containing VIII group metals, K-17and K-18 –containing VI group metals , K-5, K-6 and K-15- containing VI+VIII groups metals and K-12 industrial catalyst - Al-Ni-Mo).

Experimental results show that in the same reaction condition and the same support, the highest $H_2$ concentrations were observed on the catalysts K-3, K-7, K-9, K-10 and K-11 containing VIII group metals (Ni and/or Co). The catalysts K-17 and K-18 containing VI group metals (Cr or Mo) had the lowest activity. The catalysts K-5, K-6, K-15 and K-12 (industrial Al-Co-Mo catalyst) containing VI group (Cr and/or Mo) + VIII group ( Ni and/or Co) metals generally had less activity than the catalysts containing only VI group (Cr or Mo) or VIII group ( Ni and/or Co) metals. At the same time, catalysts containing Ni + Co (K-9 and K-11), had much higher activity compared to Ni and Co containing catalysts only (respectively K-3,

K-10 and K-7). It was also shown that the catalysts with same active metals and which were supported on γ-$Al_2O_3$ (K-9) at the decomposition of natural gas were more active than the catalyst supported on $SiO_2$ (K-11). Consequently, in the decomposition of natural gas, maximum value of $H_2$ concentration ( 91.2 mol %) was observed at 700 $^{\circ}$C on surfaces of K-9 catalyst containing %10 Ni+ %10Co on γ-$Al_2O_3$. Hydrogen concentration at 700 $^{\circ}$C on industrial Al-Ni-Mo catalyst (K-12) was about 20 mol%.

Influence of reaction temperature on the $H_2$ formation on different catalysts in the decomposition of LPG is presented in Fig. 2.
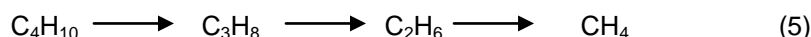


**Fig.2.** Influence of catalyst type and reaction tempera- ture on the $H_2$ formation from decomposition of LPG.

For comparison, influence of reaction temperature of the $H_2$ formation on some catalysts in direct decomposition of the pure methane is presented in Fig. 3.

The comparison of the results presented in Fig.2 and 3 with the results presented in Fig.1 confirm that generally, independent from the nature of raw materials and reaction temperature most active catalysts contained VIII group metals (Ni and/or Co). The catalysts containing VI group metals (Cr or Mo) have the lowest activity. It is also observed from Fig. 2 that compared to natural gas, at the decomposition process of LPG, K-9 and K-11, catalyst activities are especially close to higher temperatures (650 and 700 $^{o}$C). Under these conditions, catalyst K-5 shows relatively high activity and with the increase of temperature to 700 $^{o}$C its activity has not changed significantly.

The experimental results of the disruption of LPG on K-9 and K-5 catalysts are presented in fig. 4/A,B. According to the gas products to have been obtained on both catalysts it could be supposed that $C_4$, $C_3$ and $C_2$ hydrocarbons contained by LPG could turn into to methane as a result of various reactions (essentially sequential) with the increase of the temperature from 500 to 700 $^{0}$C. The relevant supposition could principally be presented as follows:

$$C_4H_{10} \longrightarrow C_3H_8 \longrightarrow C_2H_6 \longrightarrow CH_4 \qquad (5)$$

Afterwards, the obtained methane is decomposed to hydrogen and carbon directly. As shown in fig. 4, this supposition generally does not depend on the activity and type of catalysts and reaction temperature range. Since K-9 and K-5 catalysts contain different active metals, with the increase of the reaction temperature from 500 to 700 $^{o}$C, the alteration character and their ratios of produced hydrogen, methane and $C_2$– $C_4$ hydrocarbons differ.
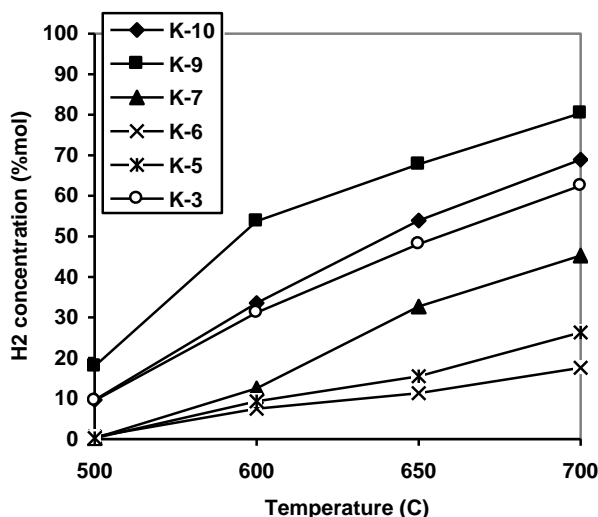


**Fig.3.** Influence of catalyst type and reaction temperature on the $H_2$ formation by direct decomposition of pure methane

Behavior of most active catalyst K-9 was studied in decomposition of natural gas in durability test. It was observed that during the initial working time of the catalyst the hydrogen concentration in gas products increased 1.8-2 times at 650$^{o}$C. This fact, as shown above, may be explained by the induction period and auto catalytically reduction of metal oxides to metals by means of hydrogen and carbon which are formed by the direct decomposition of methane. It is known that metal form in the composition of catalysts is more active in decomposition of methane. Another reason of this is considered to be as follows: irrespective of the used raw material, due to significant amounts of coke production as by product, the particles of catalysts with high activity become mechanically decomposed and their particular sizes shrink significantly (as small as dust particles) and as a result this create probable diffusion difficulties for the direct decomposition of methane or $C_2$ – $C_4$ hydrocarbons.

During next five hours the catalyst did not currently change its activity. After this time, catalysts were regenerated by means of air multiple times after coke formation. The oxidative regeneration of catalysts was realized in reactor at 650$^{o}$C and in air velocity 2000 hour $^{-1}$. In such conditions, the necessary time to fully burn the produced coke over the catalyst is observed to take nearly the same time taken at the reaction conditions of the catalyst.

Influence of number of oxidative coke regeneration on the activity of K-9 catalyst is presented in Fig. 5.

**B**
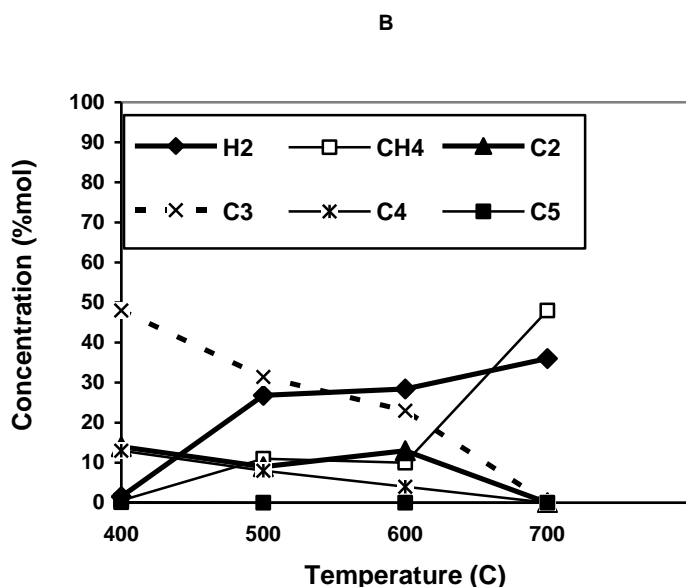


**Fig.4**. Influence of reaction temperature on the formation of $H_2$ from $C_2$-$C_4$ hydrocarbons by decomposition of LPG on K-9 (A) and K-5 (B) catalysts.

As shown in fig.5, after multiplied oxidative regeneration, the activity of the catalyst was not decreased, on the contrary after 4th regeneration it was increased form the value of 88% to 92 %. This situation has also showed that catalyst did not get poisoned from the influence of sulfuric compounds ($H_2S$, ethylmercaptane etc.) contained in natural gas and LPG (Table 1).

The character of coke, which was formed in reaction conditions, was studied by means of DTG method. The results showed that, by decomposition of natural gas and LPG, on the surface of K-9 catalyst formed about 38-40 mass% coke. In the same conditions on the surfaces of K-5 and K-6 catalysts formed 21.8 and 15.2 mass% of coke respectively. Consequently, in the same reaction conditions, more amounts of coke are formed on the catalyst with higher activity.

The DTA curves character for some catalysts are presented in fig. 6.
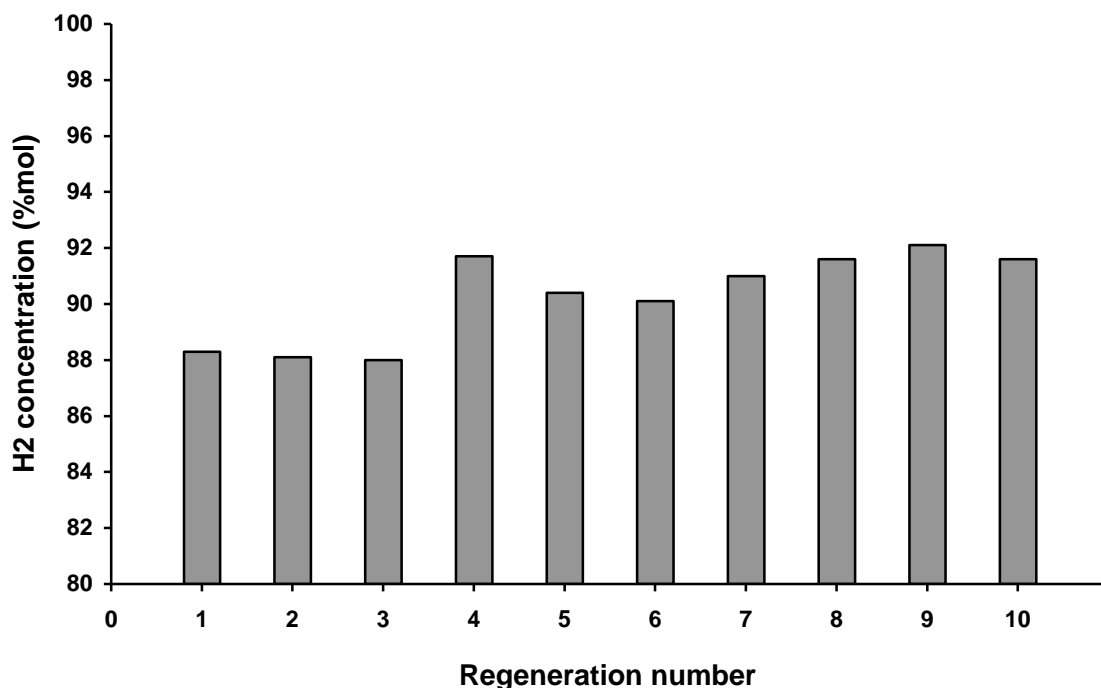


**Fig.5.** Influence of number of oxidative coke regeneration on the activity of K-9 catalyst in decomposition of natural gas.
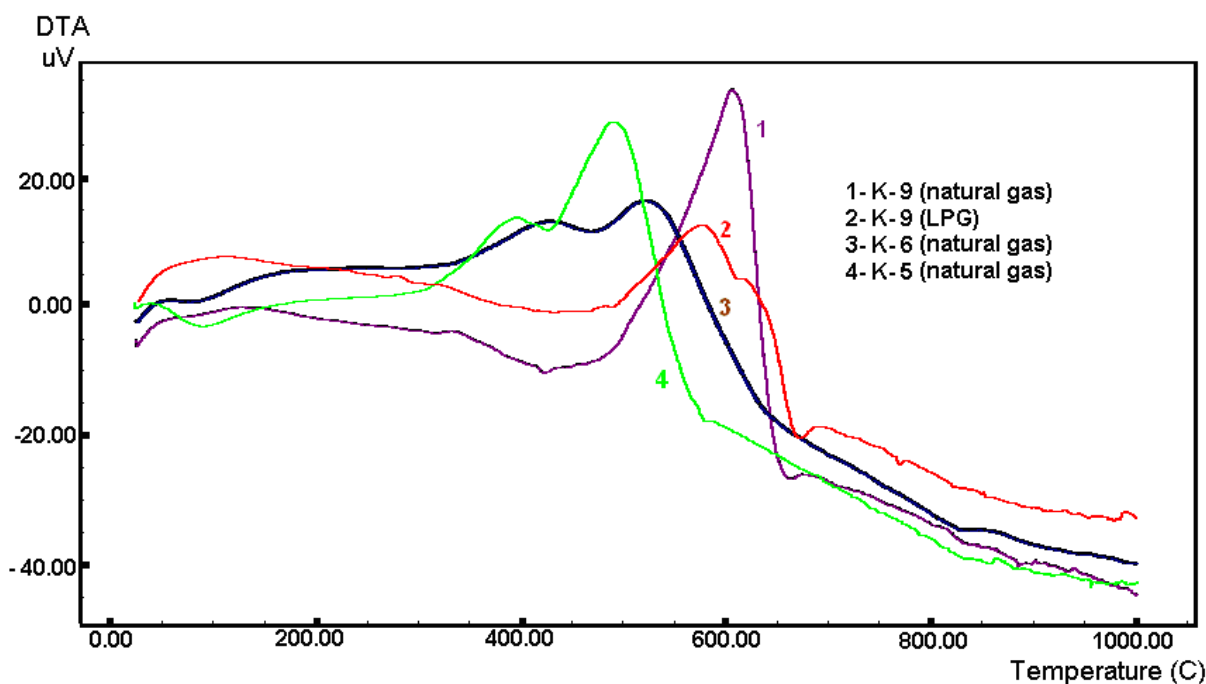
**Fig.6.** Influence of the type of catalysts on the DTA curves character.

## 4. Conclusions

Catalytic decomposition of natural gas and LPG for hydrogen production was investigated. It revealed that the catalysts containing VIII group metals (Ni and/or Co) are more active than catalysts containing VI group (Cr and/or Mo) or VI + VIII group (Cr and/or Mo + Ni and/or Co) metals. For the preparation of catalysts as a support material $\gamma$-$Al_2O_3$ is more effective in the decomposition of natural gas than $SiO_2$. Generally, for all prepared catalysts it was established that not depending on the used raw material type, by the increase of temperature from 500 to 700 $^{o}$C, $H_2$ concentration has significantly increased. The selected most active catalyst, containing VIII group metals (%10Ni + %10Co/ $\gamma$-$Al_2O_3$) after multiply oxidative regenerations did not change the activity. This catalyst also did not change (was not poisoned) its activity and stability from the influence of sulfuric compounds contained in natural gas or LPG.

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## КАТАЛИТИЧЕСКОЕ РАЗЛОЖЕНИЕ ПРИРОДНОГО И СЖИЖЕННОГО НЕФТЯНОГО ГАЗА ДЛЯ ПОЛУЧЕНИЯ ВОДОРОДА

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*Катализаторы, содержащие металлы VI группы (Cr и/или Mo) и/или VIII группы(Ni и/или Co) на носителе $\gamma$ -$Al_2O_3$, были исследованы в процессе разложения природного газа и СНГ (сжиженный нефтяной газ) в интервале температур 500-700$^o$C. Было установлено, что на катализаторах, содержащих металлы VIII группы (Ni и Co), выход водорода выше, чем на катализаторах, содержащих металлы VI группы (Cr или Mo). При разложении природного газа катализатор, содержащий Ni и Co на $\gamma$-$Al_2O_3$, в аналогичных условиях проявляет большую активность, чем на носителе $SiO_2$. Окислительная природа и масса кокса, образовавшегося на катализаторах во время реакции, были исследованы методом дифференциального термогравиметрического анализа.*

## TƏMİZ HİDROGENİN ALINMASI ÜÇÜN TƏBİİ VƏ MAYE NEFT QAZININ PARÇALANMASININ TƏDQİQİ

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*Təmiz hidrogenin alinması üçün təbii və maye neft qazının parçalanması prosesində $\gamma$ -$Al_2O_3$ daşıyıcı üzərində VI qrup (Cr və/ və yaxud Mo) və/və yaxud VIII qrup (Ni və/ və yaxud Co) metallar olan katalizatorların aktivlıyı yoxlanılıb. Müəyyən olunub ki, tərkibində Ni və Co olan katalzatorların iştirakında hidrogenin çıxımı daha yüksəkdir, nəinki Cr və Mo tərkibli katalizatorlarda. Reaksiya zamanı katalizatorun üzərində əmələ gələn koks DTQ analiz metodu ilə öyrənilib.*