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Hydrocarbon Synthesis During Methane Pyrolysis

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1. Statement of the problem

In the process of thermal-oxidative pyrolysis at a temperature of 1300-1600°C, gases, containing CO and H_2, can be produced; therefore, their conversion is reduced to catalytic hydration by Fischer-Tropsch reaction.

The Fischer-Tropsch process has become attractive due to the price rise and resulting shortage of hydrocarbons. The main disadvantage of this process is its low selectivity. Therefore, the efforts of scientists, working in this field, are focused on increasing the process selectivity to produce raw materials for the oil refining industry, as well as on development of modified catalysts that will allow to produce narrow fractions of hydrocarbons.

The catalytic conversion of pyrolysis gases (methane) may involve solutions to a number of scientific problems, including the following:

- production of organic intermediate products (ethylene, propylene),
- development of waste-free technological processes,
- production of raw materials for organic synthesis.

2. Identification of previously unsettled parts of the general problem

Paper (Gudiyella et al. 2018, Duy Khoe Dinh et al. 2019, Qi Zhang et al. 2016) presents information on the conversion of products of natural gas thermal-oxidative pyrolysis into a mixture of hydrocarbons based on Co – 6.2% wt., MgO – 7.1% wt., ZrO_2 catalyst. Since by using this catalyst, during conversion from synthesis gas to pyrolysis gas, containing 4% acetylene, a significant increase in the percentage of liquid hydrocarbon yield (up to 35%), was achieved; we think it would be relevant to study the conversion of pyrolysis gases based on other catalysts that could be applied in practice.

3. Statement of assignment and methods of its solving

The method for producing the catalyst is described in (Pavlenko & Koshlak 2015, Pavlenko & Koshlak 2017, Koshlak 2019, Pavlenko & Koshlak 2019, Dąbek et al. 2018, Dąbek et al. 2016). The experiments on pyrolysis gas conversion of into a mixture of hydrocarbons made it possible to determine the effect of their yield increase during conversion from synthesis gas ($CO:H_2 = 1:2$) to methane pyrolysis gases based on other catalysts as well. Co-catalysts (64.5 CoO-3.2 CuO-32.3 Ca $Ca(AlO_2)_2$, when used with pyrolysis gases with an acetylene content (6%), can increase the yield of liquid hydrocarbons by nearly 3 times and the yield of gaseous hydrocarbons - by more than 3 times (Table 1).

The data analysis, shown in Table 1, demonstrates that under experimental conditions at a temperature of 473 K, pressure of 0.1 MPa, and space velocity of 100 h^{-1}, for pyrolysis gases, the content of alcohols C_1-C_4 is 19 times higher than when using synthesis gas and is up to 15% wt.

Note, that with a decrease in the feed rate of pyrolysis gases (increase in contact time) from 100 h^{-1} to 60 h^{-1} hydrocarbons distribute in a different way. The yield of liquid fractions C_5-C_{18} increases.

Table 1. Effect of mixture composition on yield and distribution of hydrocarbon synthesis products

Mixture	Product yield, g/nm^3					C_1-C_4, % mass
	A_1	A_2	A_Σ	A_3	A_4	
Synthesis gas $CO:H_2 = 1:2$ (volume)	10.2	42.9	53.1	13	58.2	0.8
Pyrolysis gases C_2H_2 = 6,4% (volume)	26.9	138.8	165.7	25.5	46.1	14.5
^{1}Pyrolysis gases C_2H_2 = 6,7% (volume)	44	123	167	86	77	7.1
^{2}Pyrolysis gases C_2H_2 = 6,7% (volume)	11	92.5	103.5	16.3	38.8	6.2

^{1} – volumetric speed 70 hour^{-1},

^{2} – volumetric speed 70 hour^{-1}, catalyst after regeneration,

A_1 – liquid hydrocarbon yield C_5-C_{18},

A_2 – liquid gas yield C_1-C_4,

A_Σ – total hydrocarbon yield,
A_3 – CO_2,
A_4 – H_2O.

In our experiments, after 50 hours of operation on $CO+H_2+C_2H_2$ mixtures, the catalyst activity decreased by 7%. To restore its initial activity, the catalyst was regenerated with hydrogen at 673K (Table 2). When hydrogen is fed, the molecular layer of C-atoms is hydrated and taken off the catalyst surface in the form of methane.

Table 2. Effect of catalyst regeneration time on the composition of products (T = 673K)

Regeneration time, minutes	content of components, % volume			
	O_2	N_2	CH_4	CO_2
100	0.13	0.63	1.35	0.13
150	0.12	0.59	1.1	0.1
190	0.11	0.54	0.88	0.07
250	0.14	0.68	0.58	0.07
290	0.12	0.59	0.58	0.07

4. Study results and their discussion

The hydrocarbon synthesis process based on pyrolysis gas is characteristic of preferential yield of ethylene compared to propylene. Quantitative and qualitative distribution of olefin hydrocarbons is shown in Fig. 1.

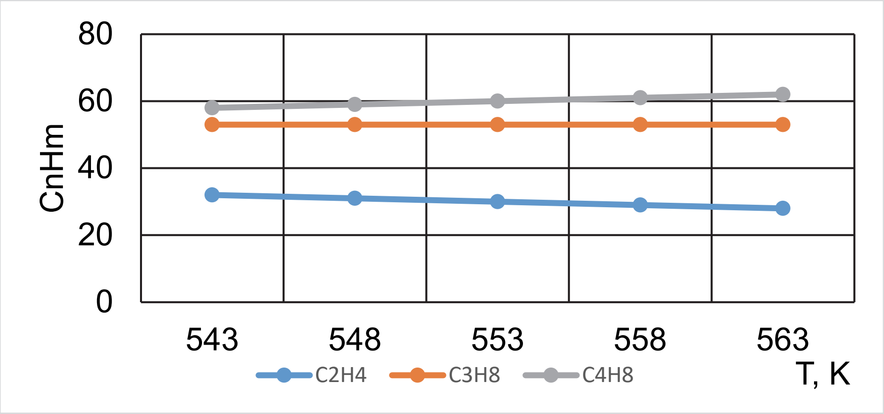

Fig. 1. Dependence of hydrocarbon yield on temperature

Based on the presented data, it follows that the main component of olefin hydrocarbons is ethylene; its proportion, with gas-synthesis temperature increase, decreases due to increase of propylene and butylene content.

Increase in the space velocity of pyrolysis gases up to 700 h^{-1} (Fig. 2) causes an increase in the amount of olefin hydrocarbons by 20%, the catalyst efficiency increases by 3 times.

Figure 2 shows the dependence of individual hydrocarbon yield on the space velocity; its analysis shows that ethylene and butylene are main hydrocarbons, methane and ethane are saturated hydrocarbons. Values within 700-740 h^{-1} ranges are considered as the optimal space velocity. Propane and butane were not among the synthesis products.

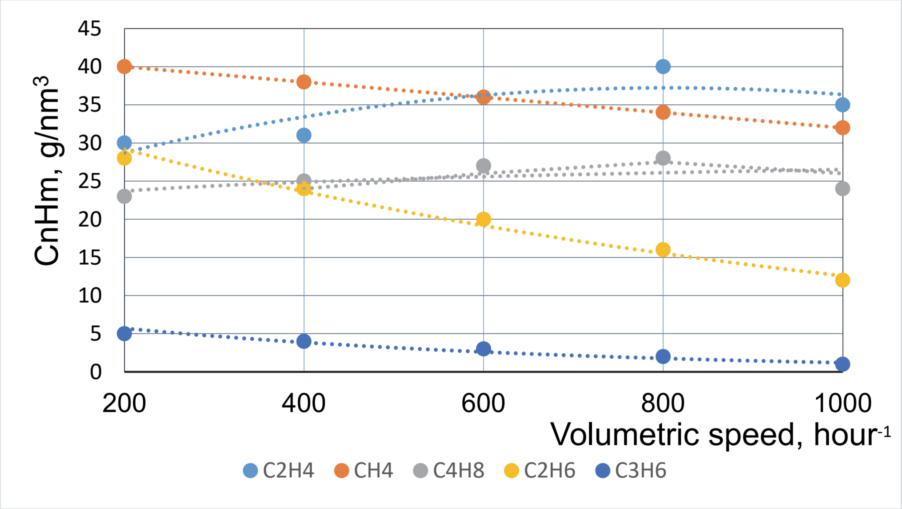

Fig. 2. Dependence of hydrocarbon yield on space velocity

The data, obtained during hydrocarbon synthesis from acetylene-containing methylene gas pyrolysis, made it possible to assert, that with acetylene in the amount of 4-5%, CO conversion decreases by 8%, compared to results of the process based on “pure” synthesis gas. At the same time, despite a decrease in CO conversion, the transition from synthesis gas to pyrolysis gas increases hydrocarbon yield, thus, making the process more selective.

A similar effect of CO conversion decrease upon introduction of unsaturated hydrocarbon additives into synthesis gas is demonstrated in paper (Hee-seok et al. 2016, Qi Zhang et al. 2016). The authors of this paper attributed this effect to competitive CO replacement by ethylene and acetylene from active catalyst surface sites. However, we assume, that increase in the total hydrocarbon yield, is related to the fact that a part of hydrocarbons is formed by means of adsorbed ethylene or acetylene.

Thus, the obtained data indicate a rather complex process of acetylene and synthesis gas interaction. Acetylene affects the degree and direction of synthesis gas conversions, interacting and participating in unsaturated hydrocarbon formation. The data analysis on methane pyrolysis gases conversion based on modified co-catalysts showed, that use of methane pyrolysis gases with 4-7% acetylene content as a basic raw material makes it possible to intensify the hydrocarbon synthesis process.

5. Conclusions

Basic laws of hydrocarbon synthesis from the pyrolysis methane gas based on modified co-catalysts were studied. The liquid hydrocarbon yield was increased by nearly 3 times, for gaseous hydrocarbon – up to 5 times when using pyrolysis gases based on modified catalyst (65% CoO-3% CuO, 32.5% Ca $(AlO_2)_2$).

It was demonstrated that the 10Co-0.4Pd/SiO_2 catalyst is selective relative to olefin hydrocarbons. In comparative conditions, at the same synthesis temperatures and catalyst load, the yield of low-molecular $C_{20}C_5$ olefin hydrocarbons for pyrolysis gases increases up to 3 times.

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Abstract

The catalyzed conversion of acetylene to higher hydrocarbons has been studied by many researchers. The importance of these processes is determined by the fact that a successful conversion of this type will create technologies for obtaining cheap alternative synthetic fuel. Acetylene can be obtained in large quantities from coal and methane, which opens up the possibility of obtaining the specified synthetic fuel. However, the lack of an effective catalyst for continuous conversion has not allowed the development of this alternative fuel route.

Features of hydrocarbon synthesis during methane pyrolysis, based on modified catalysts, are presented in the paper. It is demonstrated that production of hydrocarbons from pyrolysis gas using modified catalysts can be intensified.

Keywords:
methane pyrolysis, modified catalysts, hydrocarbons

Synteza węglowodorów podczas pirolizy metanu

Streszczenie

Katalityczna konwersja acetylenu do wyższych węglowodorów była przedmiotem badań wielu badaczy. Znaczenie tych procesów determinuje fakt, że udana konwersja tego typu pozwoli nam opracować nowe technologie pozyskiwania taniego alternatywnego paliwa syntetycznego. Acetylen można uzyskać w dużych ilościach z węgla i metanu, co otwiera możliwość uzyskania określonego paliwa syntetycznego. Jednak brak skutecznego katalizatora do ciągłej konwersji nie pozwolił na opracowanie tej alternatywnej drogi paliwowej.

W artykule przedstawiono cechy syntezy węglowodorów podczas pirolizy metanu na modyfikowanych katalizatorach. Wykazano, że można zwiększyć produkcję węglowodorów z gazu pirolitycznego na modyfikowanych Co-katalizatorach.

Słowa kluczowe:
piroliza metanu, modyfikowane katalizatory, węglowodory