

# Catalytic Decomposition of Light Hydrocarbons over a Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> Catalyst for Development of an Associated Petroleum Gas Utilization Technology

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**Abstract**—The decomposition of light hydrocarbons with use of a Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst and the production of carbon nanomaterials and hydrogen as the main process products is proposed in this work for the utilization of associated petroleum gas in small and distant oil fields. It was found that a 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst is most effective in the decomposition of a propane–butane mixture in a temperature range of 700–725°C; under these conditions, to 700–750 L of H<sub>2</sub> per gram catalyst can be obtained. The concentration of hydrogen at the reactor outlet was 70–75 mol %.

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## INTRODUCTION

Associated petroleum gas (APG) is considered a by-product of oil extraction; in the absence of a possibility of its processing, it is simply flared [1, 2]. In the combustion of APG, tons of pollutants are released into the atmosphere every year to worsen ecological situations in oil-field regions. In this case, significant amounts of valuable chemical raw materials are lost because, unlike natural gas, APG contains ethane, propane, butane, and nonhydrocarbon gases.

All operations involving APG are currently regulated for the most part by federal law no. 69-FZ of March 31, 1999, “On Gas Supply in the Russian Federation”; however, there are no subordinate regulations specifying the positions of this law with respect to APG, and APG is not legally considered as a separate fossil fuel. Nevertheless, governmental regulation no. 1148 of November 8, 2012, “On the Emission Charge for Pollutants Formed on Flaring and (or) of Dissipation Associated Petroleum Gas” became effective IN January 1, 2013. Because APG is a valuable chemical raw material and highly efficient organic fuel, there are two directions of its use: power-generating and petrochemical applications.

In this work, we propose a method for the catalytic decomposition of C<sub>1</sub>–C<sub>4</sub> hydrocarbons with the production of carbon nanomaterials and hydrogen as the main products in order to improve geoecological situations in oil-field regions and to utilize APG. The application of this method makes it possible to obtain a gas mixture with a high hydrogen content and free of carbon oxides; because of this, the separation of

hydrogen is facilitated. Previously [3], we described the use of a Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst for the decomposition of methane. The study of the properties of this catalyst in the decomposition of other hydrocarbons can extend the range of its application. In this work, we report results of studying the Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the decomposition of a propane–butane mixture over a temperature range of 650–750°C.

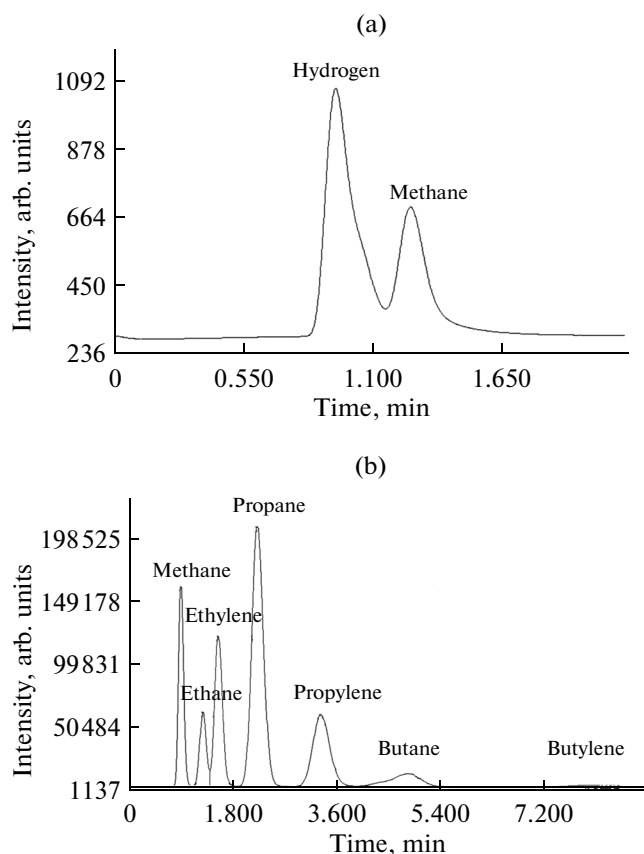
## EXPERIMENTAL

### *Preparation of the Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> Catalyst and Experimental Procedures*

The Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained by the mechanochemical activation of a mixture of oxides (Fe<sub>2</sub>O<sub>3</sub>, NiO, and CuO) with aluminum hydroxide (hydrargillite) in an AGO-2 centrifugal planetary mill (Novits, Russia; the rotational velocity of drums was 10 s<sup>-1</sup>). Initially, the experiments were performed in a quartz flow reactor with a McBain balance; this made it possible to determine the main rate laws of the formation of carbon deposits on the catalysts. Then, the catalyst was tested in a system with a rotating reactor.

### *Experimental Procedure in the System with a Rotating Reactor*

The reactor in the form of a tube was arranged in a horizontal furnace [4]. Before the beginning of the synthesis, the catalyst was loaded at the center of the horizontally arranged reactor. The reactor was heated in an inert gas (argon) flow to the preset temperature with the aid of an electric furnace. The catalyst was



**Fig. 1.** Chromatograms of the gas mixture at the reactor outlet upon the decomposition of a propane–butane mixture at 700°C in the absence of a catalyst: (a) thermal conductivity detector (TCD) and (b) flame-ionization detector (FID).

stirred on the periodic rotation of the reactor to facilitate the uniform formation of hydrocarbon material. A propane–butane mixture was supplied at the reactor inlet. The catalytic reaction of the production of hydrogen and carbon nanomaterial occurred in the high-temperature zone. The composition of a gas mixture was analyzed with the aid of a Kristall 2000 gas chromatograph (Kupol, Russia).

**Table 1.** Composition of a gas mixture at the reactor outlet upon the decomposition of a propane–butane mixture (feed rate, 6.5 L/h) in the absence of a catalyst at 700°C

Gas	Gas fraction in the mixture, vol %
Hydrogen	10
Methane	26
Ethane	6
Ethylene	14
Propane	28
Propylene	12
Butane	3
Butylene	1

## RESULTS AND DISCUSSION

### *Pyrolysis of a Propane–Butane Mixture in the System with a Rotating Reactor without a Catalyst*

Before performing the catalytic decomposition of a propane–butane mixture in the system with a rotating reactor, we studied the occurrence of pyrolytic transformations. For this purpose, a propane–butane gas mixture was supplied to the reactor without a catalyst heated to 700°C. The experiment was performed for 6 h. At 700°C, bond breaking occurred in the molecules of propane and butane with the formation of methane, C<sub>2</sub> hydrocarbons, and an amount of hydrogen (~10%). Figure 1a shows the chromatogram of an analyzed gas mixture at the reactor outlet; the analysis was performed with the use of a thermal conductivity detector (TCD). This analysis makes it possible to calculate the fraction of hydrogen in the gas mixture. Based on the chromatographic analysis carried out with the use of a flame-ionization detector (FID) (Fig. 1b), it is possible to calculate the ratios between hydrocarbon gases in the mixture.

Table 1 summarizes the ratios between gaseous products at the reactor outlet after the pyrolysis of a propane–butane mixture at 700°C.

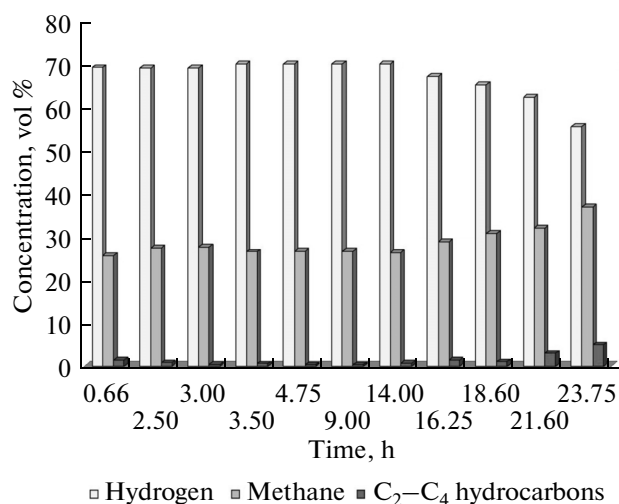
From the above data, it follows that the thermal pyrolysis of the propane–butane mixture occurred intensively in the empty reactor. The fairly small proportion of hydrogen (at most 10%) indicates that pyrolysis makes an insignificant contribution to hydrogen formation. Olefins (ethylene and propylene), which exhibit higher activity in the formation of carbon nanofibers than saturated hydrocarbons, were present among the main products of pyrolysis.

### *Testing of the 70%Ni–10%Cu–10%Fe/Al<sub>2</sub>O<sub>3</sub> Catalyst in the Decomposition of a Propane–Butane Mixture in the System with the Rotating Reactor*

In the series of experiments carried out at 650–750°C, the catalyst load was 0.5 g. The catalyst was loaded at the center of the reactor, and the reactor was slowly revolved at a zero inclination angle. Thus, the catalyst only revolved around the axis of the reactor without its displacement along the reactor. Additional supply was not performed because the catalyst was stable. The experiments were carried out for 25–30 h.

At 650°C, the main reaction products in the first 15 h were hydrogen (55–60 mol %), methane (36–40 mol %), and propane (3–4 mol %). Then, the concentration of hydrogen gradually decreased to indicate a decrease in the catalyst activity. Simultaneously, the concentration of C<sub>2</sub>–C<sub>4</sub> hydrocarbons increased to indicate an increase in the contribution of thermal pyrolysis reactions to the conversion of the propane–butane mixture. The yield of carbon nanofibers after 30 h of reaction was 220 g/g.

As the reaction temperature was increased to 700°C, the conversion of the propane–butane mixture increased. From Fig. 2, it follows that the concentra-



**Fig. 2.** Changes in the composition (vol %) of the reaction products of the decomposition of a propane–butane mixture with time at 700°C.

tion of hydrogen at the reactor outlet was 71–72 mol %, the concentration of methane was 25–26 mol %, and the concentration of C<sub>2</sub>–C<sub>4</sub> hydrocarbons was 1–2 mol % (the space velocity of a C<sub>3</sub>H<sub>8</sub>–C<sub>4</sub>H<sub>10</sub> feed mixture was 12000 h<sup>-1</sup>). The volume of the reaction mixture at the reactor outlet increased from 6.4 to 21 L/h, that is, by a factor of about 3.3. The volume of the reaction mixture increased primarily due to the occurrence of the decomposition of propane, the main component of the propane–butane mixture. The 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst stably operated at 700°C for a long time (~800 min). The concentration of hydrogen gradually decreased after 13–14 h of reaction, and the concentration of methane and C<sub>2</sub>–C<sub>4</sub> hydrocarbons increased. This is indicative of a

decrease in the contribution of the catalytic decomposition of the propane–butane mixture to the conversion of the initial C<sub>2</sub>–C<sub>4</sub> hydrocarbons.

During the steady-state catalyst operation, the composition of gas mixture at the reactor outlet changed insignificantly (Fig. 2).

The gradual decrease of methane concentration after 13 h of reaction and an increase in the concentrations of other hydrocarbons (especially, ethane and propane) indicate a decrease in the catalyst activity.

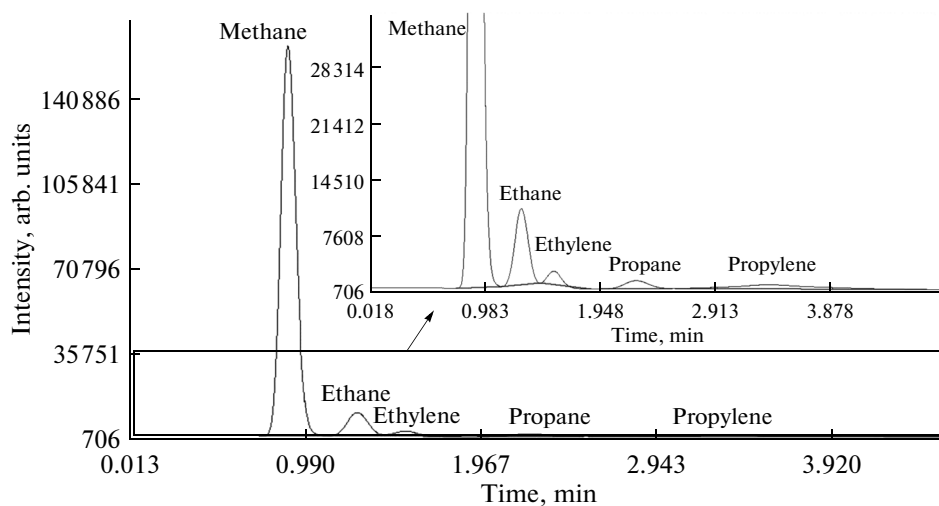
Figure 3 shows the chromatogram of hydrocarbon products at the point in time  $\tau_{\text{react}} = 40$  min. It is evident that methane is the main hydrocarbon product of the reaction.

Table 2 summarizes the composition of the gas mixture (reaction products) at the reactor outlet upon the decomposition of the propane–butane mixture at 700°C at the point in time  $\tau_{\text{react}} = 40$  min.

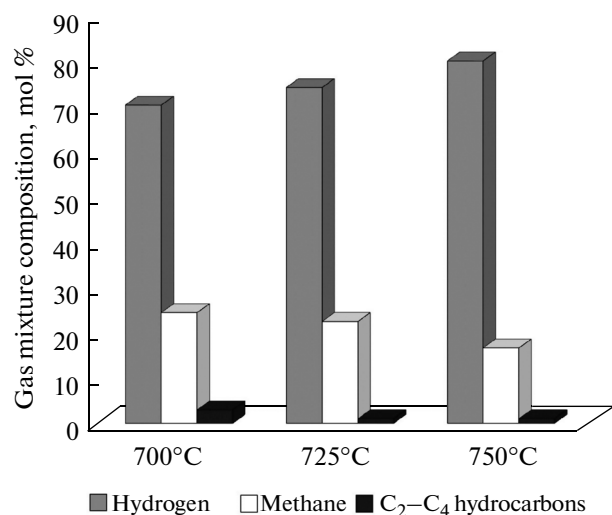
Analogous results were obtained upon the decomposition of the propane–butane mixture performed at 725 and 750°C.

The histogram in Fig. 4 shows that, as the temperature was increased to 725°C, the operational stability of the catalyst decreased only slightly to 12–13 h. The concentration of hydrogen at the reactor outlet increased to 75–76 mol %, and the concentration of methane decreased to 22–23 mol %. The yield of carbon nanofibers after 26 h of reaction was 350 g/g.

As the reaction temperature was increased to 750°C, the concentration of hydrogen at the reactor outlet increased to 81–82 mol %, and the concentration of methane decreased to 16–17 mol %; however, the operational stability of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst sharply decreased to 5–5.5 h. The yield of carbon nanofibers after 8 h of reaction was 50 g/g at the space velocity of the supply of the propane–butane mixture of 12000 h<sup>-1</sup>.



**Fig. 3.** Chromatogram of the hydrocarbon products formed upon the decomposition of a propane–butane mixture at 700°C ( $\tau_{\text{react}} = 40$  min).



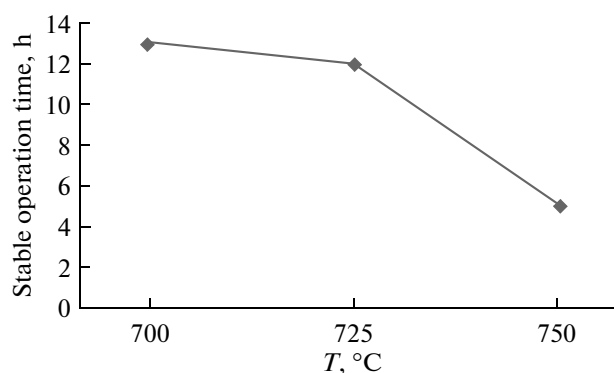
**Fig. 4.** Dependence of the gas mixture composition at the reactor outlet upon the decomposition of a propane–butane mixture on the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst upon reaction temperature.

Thus, we can conclude that an optimum temperature range for the production of hydrogen and carbon nanofibers from a C<sub>3</sub>H<sub>8</sub>–C<sub>4</sub>H<sub>10</sub> mixture on the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the system with a rotating reactor is 700–725°C. Upon performing the decomposition of a propane–butane mixture under the optimum process conditions, 700–750 L of H<sub>2</sub> and 320–350 g of carbon nanofibers per gram of catalyst can be obtained. Figure 5 shows the temperature dependence of the time of stable catalyst operation, from which it follows that the stability of the catalyst decreased with an improvement in other process characteristics as the temperature was increased. With an increase in the temperature from 725 to 750°C, the time of stable catalyst operation halved.

The results of the experiments showed that, upon the decomposition of propane and butane, a gas mix-

**Table 2.** Composition of the gas mixture at the reactor outlet at the pint in time  $\tau_{\text{react}} = 40$  min upon the catalytic decomposition of a mixture of C<sub>3</sub>H<sub>8</sub>–C<sub>4</sub>H<sub>10</sub> at 700°C

Gas	Gas fraction in the mixture, vol %
Hydrogen	72
Methane	25
Ethane	2
Ethylene + propane/propylene + butane	1



**Fig. 5.** Dependence of the stable operation time of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the decomposition of a propane–butane mixture upon reaction temperature.

ture of hydrogen and C<sub>1</sub>–C<sub>4</sub> hydrocarbons was formed at the reactor outlet; therefore, for the subsequent use of hydrogen, it should be purified to remove methane and propane–butane mixture residues.

Thus, the above studies demonstrated the effectiveness of the operation of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the decomposition of a propane–butane mixture in the system with a rotating reactor. At a propane–butane mixture space velocity of 12000 h<sup>-1</sup>, the optimum temperature range was 700–725°C. Under these conditions, the yield of 700–750 L of H<sub>2</sub> per gram of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained. The concentration of hydrogen at the reactor outlet was 70–75 mol %.

This method of the catalytic decomposition of light hydrocarbons can be used in prospect as a stage in the development of an associated petroleum gas utilization technology in small and distant oil fields.

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