





Decomposition of light hydrocarbons on a Ni-containing glass fiber catalyst

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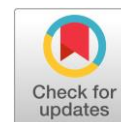
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Abstract

The work is devoted to the study of the novel process of catalytic decomposition of light hydrocarbons on a catalyst at temperatures of 550 °C and 600 °C at various pressures. The CVD process is a new CO_x-free approach for hydrogen production. A glass fiber fabric was used as a catalyst, which was preliminarily modified by the application of additional outer layers of NiO and porous silica. A technical mixture of propane and butane was used as feedstock. The main purpose is to investigate the effects of pressure and temperature on the production of hydrogen and carbon nanofibers over a glass-based catalyst. As a result of the decomposition of the mixture, the yield of hydrogen was 266–848 L/g_{cat}, and that of carbon nanofibers was 3–10 g/g_{cat}. Increasing the pressure of propane-butane mixture decomposition led to an increase of the catalyst lifetime. The highest yield of hydrogen and carbon nanofibers was achieved at 1 bar and 600 °C.

Keywords

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Key findings

- The effect of temperature (550, 600 °C) and pressure (1, 2 atm) on the conversion of a propane-butane mixture was studied.
- Novel data on hydrogen synthesis via methane decomposition at pressure higher than 1 atm.
- Dynamics of catalyst deactivation was investigated.

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1. Introduction

Due to the constantly increasing demand for energy resources that meet modern environmental standards, the development of alternative and renewable energy sources to replace traditional fuels is an urgent task for the world scientific community [1–2]. The most promising and likely scenario for solving this problem is the formation of a hydrogen economy, where hydrogen is a universal energy carrier commensurate with oil, gas and coal. In many respects, hydrogen is superior to other types of fuels, for example, high efficiency (the efficiency of power plants is 80–90%), high environmental friendliness (exhaust gases when it is used as a fuel consist of water vapor), versatility (the ability to accumulate energy obtained from other alternative and renewable sources). According to various forecasts, this could happen worldwide after 2040, but in some regions, the hydrogen economy is already taking

shape today [3]. To use hydrogen as an automotive fuel at compressed natural gas (CNG) filling stations, it is necessary to deliver it to the consumer. It is possible to deliver it in cylinders (at pressures up to 700 atm), but this is an energy-intensive process. A more efficient approach is to transport hydrogen in a bound state, for example, in the form of hydrocarbons and produce hydrogen directly on site [4]. Two types of readily available hydrocarbon-containing gases can be used as sources at CNG filling stations: natural gas and technical propane-butane mixture (PBM). A methane/PBM catalytic converter is installed directly at the CNG filling station to produce hydrogen in the required amount. Previously, the authors of [5] showed that a glass fiber-based nickel catalyst is active in the decomposition of methane and light hydrocarbons at a temperature of 450 °C and atmospheric pressure. PBM is a cheap, easily transportable raw material with safe storage, since it does not require high pressures. The second prod-

uct which is formed during methane decomposition is nanofibrous carbon [6–8]. There are a variety of its applications, and the investigation of such a material is of increasing interest [9–14]. Therefore, in this work, we studied the effects of temperature (550, 600 °C) and pressure (1–2 atm) on the conversion of a propane-butane mixture.

2. Experimental

The catalyst support was KT-11-TO high-silicon fiberglass fabric (manufactured by Stekloplastik, Zelenograd, Russia) containing ~95 SiO₂ and 4 Al₂O₃ (wt%). The glass fabric was impregnated with an aqueous solution of silica sol (type K-1, NPO IREA, Moscow, Russia) and nickel acetate. After impregnation and drying, the glass fabric was subjected to heat treatment by heating from 25 to 500 °C. The addition of silica was necessary to create an intermediate layer of a secondary porous substrate in order to improve the adhesion strength between the NiO surface and the glass fabric, while increasing the availability of gaseous reagents to the active compound NiO [15]. Using the method of transmission microscopy, it was determined that the distribution of particles is uniform, the average size of NiO particles was 15 nm [5].

The experiments were carried out on an Autoclave Engineers BTRS-Jn catalytic unit in a metal tubular reactor. The catalyst was coiled and placed in a metal flow reactor (Figure 1) in an argon flow at a rate of 1.2 L/h. The reactor was thermally stabilized at $T = 550\text{--}600$ °C. The propane-butane technical mixture according to GOST 20448-90 was used as a feedstock.

Experiments on the decomposition of PBM were carried out at pressures of 0.1–0.2 MPa with a specific consumption of methane at the inlet of 100 L/(h·g_{cat}). The concentration of gaseous products was measured on a Chromatek-Kristall 5000 gas chromatograph equipped with a thermal conductivity detector, a flame ionization detector, and an HP-AL/KCL 50 m × 0.32 mm × 8 μm capillary column (P/N 19091P-K15).

The microstructure of carbon nanofiber samples was studied by scanning electron microscopy (SEM) with field emission on a Hitachi SU8000 electron microscope. The images were taken in the secondary electron recording mode at an accelerating voltage of 2 kV and a working distance of 4–5 mm. The textural characteristics of the obtained nanofibrous carbon samples were studied by low-temperature nitrogen adsorption at 77 K on a Quantachrome NOVA 1000e adsorption unit. The specific surface area (A_{BET}) was calculated by the BET method. The specific surface of the pores remaining after the adsorbate filled the micropores (A_{T}) and the volume of micropores (V_{T}) were calculated by the comparative t-method of de Boer and Lippens, for which the statistical thickness of the adsorption film for which was calculated using the de Boer equation. The method is based on a comparison of the increments of adsorption values on the adsorption isotherm

under study and the standard adsorption isotherm obtained on well-characterized non-porous materials. In the field of polymolecular adsorption, after the filling of micropores and other specific centers, these increments of adsorption are proportional to the surface, regardless of its detailed chemical nature.

3. Results and Discussion

Previously [5], it was shown that a Ni-containing glass fiber-based catalyst is active in the decomposition of methane and light hydrocarbons at a temperature of 450 °C and atmospheric pressure. In this work, the effect of temperature and pressure on the conversion of a propane-butane mixture was studied. Figure 2 shows the results of the catalytic decomposition of PBM at a temperature $T = 550$ °C and a pressure $P = 1$ atm.

The maximum volume concentration of hydrogen was 49.7 vol% after 1 h of catalyst operation. The volume concentration of methane at the beginning of the work was 51.8 vol% and reached 0 vol% after 6.5 h of the process.

The catalyst worked under these conditions for 35 h without loss of activity, and the nonlinear change in the volume concentrations of the reaction products after 16 h of operation of the glass-fiber catalyst is associated with the carbon formation at the active centers of the catalysts.

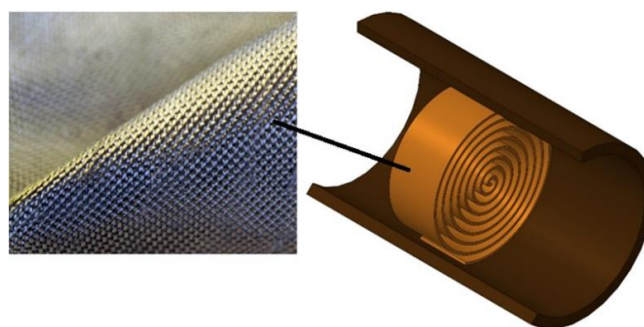


Figure 1 Appearance of glass fiber catalyst layer.

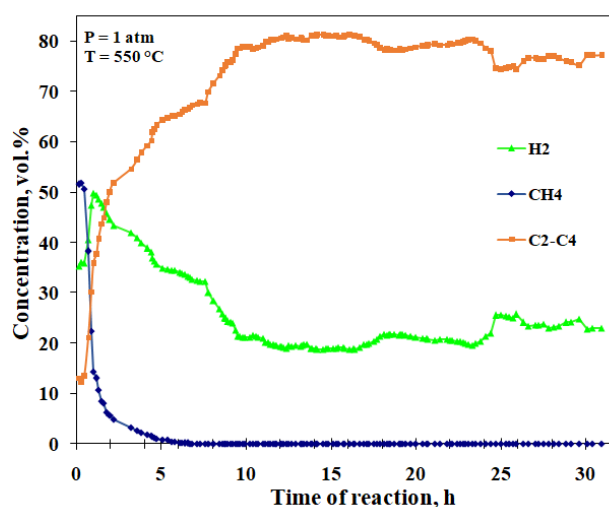


Figure 2 Change in the volume concentrations of the reaction products depending on the reaction time (1 atm, 550 °C).

The hydrogen yield in this experiment was 636 L/g_{cat} with a nanofiber carbon value of 3 g/g_{cat}. It can be seen from the data in Figure 3 that an increase in temperature to 600 °C leads to an increase in the maximum volume concentration of hydrogen to 58 vol% and within 34 h of operation of the catalyst, it decreased to 34 vol%.

The conversion of PBM under these conditions was 40.63 vol%. The yield of hydrogen in this experiment reached its maximum value and amounted to 848 L/g_{cat}, the yield of carbon nanofibers was 10.5 g/g_{cat}.

An increase in pressure to 2 atm at a process temperature of 550 °C leads to a slight decrease in the hydrogen concentration, which amounted to 25.9 vol%, reaching its maximum value of 44.7 vol% and remains approximately unchanged for 5.5 h. In this case, a slight increase in pressure in the system was observed due to the carbonization of the catalyst. The hydrogen yield in this experiment was 420.3 L/g_{cat}, while the nanofibrous carbon yield was 5 g/g_{cat}.

Figure 4 shows the change in the volume concentrations of the reaction products depending on the reaction time at a temperature $T = 600$ °C and a pressure $P = 2$ atm. Figure 4 shows that with an increase in pressure to 2 atm at a process temperature of 600 °C, the hydrogen concentration gradually increases from 43.6 vol% and reaches its maximum value of 62.7 vol% after 3 h of the experiment.

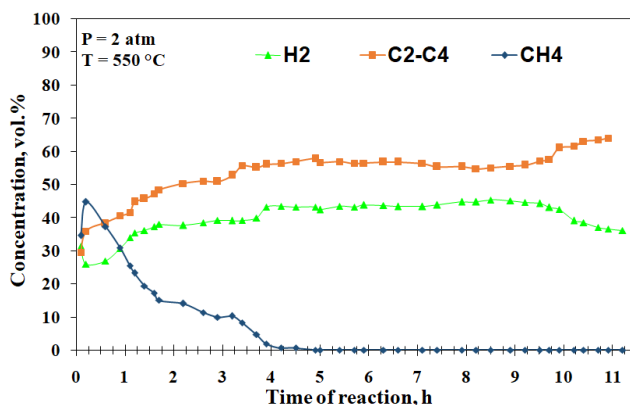


Figure 3 Change in the volume concentrations of the reaction products depending on the reaction time (1 atm, 600 °C).

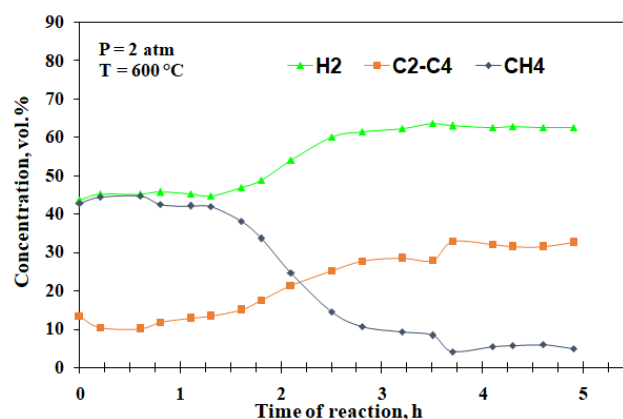


Figure 4 Change in the volume concentrations of the reaction products depending on the reaction time (2 atm, 600 °C).

The yield of hydrogen in this experiment was 266.5 L/g_{cat}, carbon nanofibers was 3 g/g_{cat}. It is important to note that under these conditions, the catalyst surface was rapidly carbonized and the experiment time was reduced to 5 h.

Table 1 presents data on the integral yields of hydrogen and nanofibrous carbon under various conditions. It can be seen that the yields of hydrogen and nanofibrous carbon reach their maximum values during the catalytic decomposition of a commercial propane-butane mixture at a pressure of one atmosphere, a temperature of 550–600 °C and amount to 636 L/g_{cat} and 848 L/g_{cat}, respectively.

It is known that the activity of a reaction catalyst directly depends on the amount of Ni in the catalyst [16]. In [17], the influence of the catalyst composition on the conversion of propane with the production of hydrogen 7–108 mol H₂/g_{cat} was studied. However, it should be noted that the nickel content was 40–50% with the addition of promoting additives (Cu, Mo). The authors of [18] decomposed light C₁–C₄ hydrocarbons and their mixtures on a catalyst of complex composition 15%Ni·5%Co·5%Fe·5%Cu·2%Mo/VCC, obtaining data comparable to this work. Whereas in this work, 12–38 H₂/g_{cat} was obtained on low-concentration monometallic systems [19–22]. At the same time, a glass fiber-based catalyst has a number of advantages over a granular catalyst, such as higher mechanical strength and ease of transportation, organization of loading into the reactor virtually eliminates gas leakage through its bed [23]. The conditions for the process of decomposition of the propane-butane mixture do not greatly affect the structure of the resulting carbon. Table 2 shows typical textural characteristics of the resulting carbon product.

4. Limitations

The further issues will be linked with the development of pilot plants for catalytic decomposition of methane or C₁–C₄ hydrocarbons over fiberglass catalysts. The reaching of optimum activity of catalysts will be achieved by creating new nanoparticle-based fiberglass systems with enhanced conversion of C₁–C₄ hydrocarbons.

5. Conclusions

Thus, the results of the experiments showed that the glass fiber material coated with nickel has prospects for application in the process of catalytic pyrolysis of light hydrocarbons, for example, PBM, and can be used as a catalyst in the utilization of associated petroleum gases. The most efficient process for the catalytic decomposition of light hydrocarbons on a Ni-containing glass fiber catalyst is the catalytic decomposition of a technical propane-butane mixture at a temperature of 600 °C and a pressure of 2 atm, but due to the high rate of carbonization of the catalyst surface, research should be continued with optimization of the process: introduce a promoting additive and/or select the experimental conditions.

Table 1 The influence of temperature and pressure of the process on the maximum volume concentration of hydrogen, the yield of hydrogen and carbon during the experiment (the PBM was used as a feedstock).

Pressure, atm	Temperature, °C	C(H ₂) _{max} , vol.%	η(H ₂), L/g cat.	η(C), g/g _{cat}
1	550	49.7	636.1	3
1	600	58.0	848.0	10.5
2	550	44.7	420.3	5
2	600	62.7	266.5	3

Also, a great advantage of carrying out the process of catalytic decomposition of PBM at 600 °C and a pressure of 1 atm is the highest yield of hydrogen $\eta(\text{H}_2) = 848 \text{ L/g}_{\text{cat}}$ and carbon nanofibers was $\eta(\text{C}) = 10.5 \text{ g/g}_{\text{cat}}$. The future studies will be devoted to estimating the effect of higher pressures (above 5 bar) and ways to enhance the hydrogen yield.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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