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Steam conversion of C$_2$-C$_4$ alkanes in a microchannel reactor

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Abstract. Steam reforming of C$_2$-C$_4$ alkanes was studied in annular catalytic reactor under atmospheric pressure over Rh-(La$_2$O$_3$, BaO)-Al$_2$O$_3$ catalysts. Effects of temperature have been compared for different residence time. Concentrations of the products of chemical reactions in the outlet gas mixture are measured at different temperatures of reactor. It was found that the catalyst has good performance and provide equilibrium product distribution at GHSV = 30000–55000 h$^{-1}$.

1. Introduction
Steam and dry reforming of hydrocarbons (mainly methane) is the main way of hydrogen and syngas production [1, 2]. Steam methane conversion occurs on different catalysts, the most active of which is rhodium [2-8] at a temperature of 700-800 $^\circ$C. The development of the chemistry of lower alkanes (saturated hydrocarbons) is due to the need to use natural and associated gases more as raw materials for the chemical industry because of the inevitable reduction in the amount of oil produced. Liquefied petroleum gas (LPG), which mainly contains propane, is a promising alternative energy source for H$_2$ production because LPG is condensed at higher temperatures than natural gas. Catalytic steam conversion of C$_2$-C$_4$ alkanes occurs at lower temperatures (500-600 $^\circ$C) than steam methane conversion [9-13]. The main products of reforming are hydrogen, carbon oxide, carbon dioxide and methane. The main task that must be solved is the selection of the catalyst, the technology of its application, and the creation of a reformer-reactor.

The creation of catalytic reactors on mini and microchannel heat exchangers gave impetus to the development of new possible devices for the production of hydrogen and syngas [5, 7, 9]. It was experimentally shown in [4-5] that it is possible to carry out the process of steam conversion of methane, partial oxidation of methane with a contact time of less than 1 ms.

When carrying out steam conversion of hydrocarbons, catalysts containing Ni or an element from the group of noble metals supported on oxide systems are used. Nickel-based catalysts are promising for the reaction because of their low cost and high catalytic activity, but are sensitive to carburization and are not selective (the concentration of CH$_4$ in synthesis gas can reach 20%), and they are low-productivity. The texture modification of nickel-based catalysts has been extensively studied to achieve high catalytic performances in steam reforming reactions. It is known that the nature of the metal-support interaction is one of the key factors that determine the properties of the deposited metal-containing particles. In particular, the chemical composition of the support can influence the size, morphology, electronic and oxidation-reduction properties of the supported metal-containing particles.
and, accordingly, on their catalytic properties. To reduce the course of coking reactions, Ni is modified by Cu, Mn, Ba, Mg, Ce, [14-18]; elements from the group of noble metals.

Elements from the group of noble metals (Ir, Ru, Pt, Rh) are widely used as catalysts for steam reforming of hydrocarbons [3-9,19-21], but Rh is considered to be one of the most suitable for the steam conversion of hydrocarbons [5-7,9,20,21]. The catalysts of noble metals are characterized by high productivity (GHSV = Reactant Gas Flow Rate/Reactor Volume can be more than 100 000 hr⁻¹), resistant to carbonization, high selectivity.

Hydrogen and syngas production in a micro-reactor from propane and water was demonstrated in [9, 13]. The development of microchannel catalysis has shown the possibility of hydrogen formation at lower temperatures from a mixture of propane and methane to produce hydrogen [13], while the conversion of propane on the nickel catalyst occurs with the formation of both synthesis gas and methane. The possibility of obtaining a syngas and hydrogen from butane in a micro-reactor was carried out in [11].

The mechanism of steam reforming reactions depends significantly as on the nature of the active metal and auxiliary material as on the inlet mixture of gases. The interactions of different hydrocarbon molecules will exert influence on each other, and their transformations will correspondingly differ from the transformations of individual elements of hydrocarbons. The purpose of the paper is to determine the degree of conversion of C₂-C₄ alkanes (LPG) to syngas at different temperatures and contact times in a microchannel annular reactor, with rhodium catalysts on a γ-Al₂O₃ support, doped with lanthanum and barium.

2. Experiment

2.1. Catalyst Preparation
The catalyst has a homogeneous fraction of noble metal nanoparticles and the optimal oxygen mobility in the support lattice. When preparing the catalyst, its support, γ-Al₂O₃ with a specific surface area of 150–170 m²/g, was impregnated with solutions of nitrate salts of lanthanum and barium (La(NO₃)₃ 6H₂O and Ba(NO₃)₂) subjected to high-temperature calcination at 1050 °C. The introduction of La₂O₃ and BaO markedly enhances the thermal stability of the catalyst, reduces the sintering rate, and slows down γ-Al₂O₃ transformation into other phases. The doped support was impregnated with an aqueous solution of Rh(NO₃)₃ so that the amount of pure metal was 5% of the support weight, calcined at 500°C. The metal rod was treated with acetone for degreasing, etched in 1M hydrochloric acid at 60°C. Then it was densely coated with titanium oxide from a complex organic solution to prevent oxidation of the metal surface at high temperatures of the steam reforming process [6, 8].

Figure 1. TEM picture of the catalyst for the steam reforming.
The aerosol spraying procedure of the catalyst was repeated many times until the required weight was reached. To avoid cracking of the applied layer, the final calcination was carried out at a rate of temperature rise of not more than 3°C / minute. A typical structure of the support (aluminum oxide) with rhodium nanoparticles inserted into its crystal lattice is shown in figure 1.

2.2. Experimental Equipment.
Experiments on the steam conversion of light hydrocarbons were carried out on the apparatus described in [6, 7] for three contact times of 65, 82, 109 ms with a steam-to-carbon ratio of five. A mixture of hydrocarbon gas and water, set by the Bronkhorst HI-TECH mass flow gas and liquid controllers, was supplied to a preheating chamber where evaporation of water, heating of water vapor and hydrocarbon gas occurred. The composition of the fuel gas (C₃H₈ -58, C₂H₆-16, n-C₄H₁₀-13, i-C₄H₁₀-12, CH₄-1% vol.) was measured before each experiment. Then the mixture of gases entered the annular reactor, where a catalytic reaction occurred on the outer surface of the inner cylinder. For heating the reactor to the reaction temperature and for stabilizing the temperature during the reaction, the reactor was placed into an electrically heated quartz tube coated with a heat-insulating material for preventing heat loss. The outlet gas mixture ran through a cooler–condenser where the water steam was condensed and the moisture separator, and the dry gas mixture was fed for analysis to gas chromatograph. In the course of the experiments, gas flow rates, reactor temperatures, and the composition of the inlet and outlet gas mixtures were measured. The temperature of the reactor was measured by a thermocouple K of the type. The reaction products were analyzed with a Perkin Elmer gas chromatograph and a gas chromatograph with an Agilent mass selective detector.

3. Experimental Results
Dry C₂-C₄ steam reforming products are represented in figure 2 as a function of temperature for contact time of 82 ms. At temperatures above 550°C, more than 60% of the hydrogen in these conversion products is observed.

![Figure 2](image-url)

**Figure 2.** Concentrations of the output gases of the steam conversion of a mixture of hydrocarbon gases on the temperature at a contact time of 82 ms. Lines correspond to equilibrium gas concentrations.
Analogously to the data obtained earlier and calculations based on the equilibrium model, an increase in the concentration of carbon monoxide with increasing reactor temperature is observed. The equilibrium calculated concentrations are given by the lines in the figure. There is also a slight decrease in the concentration of carbon dioxide in the temperature range 550 - 800°C.

Figure 3a shows the degree of steam conversion of ethane $X_{Et}$, on the temperature in the annular reactor at different contact times ($X_{Et} = (n_{Et, in} - n_{Et, out}) / n_{Et, in}$, where $n_i$ is the molar flow rate). Reducing the contact time leads to a decrease in liquid hydrocarbon conversion. An increase in the number of carbon atoms in their vapor conversion leads to a more efficient reforming process at the same temperatures.

Figure 3b shows the degree of conversion of isobutane from the temperature in the annular reactor, which is determined in the same way as ethane conversion. The degree of conversion of isobutane is greater than for ethane for the same reactor temperature. Like the conversion of isobutane, there is a steam conversion of n-butane. The calculated conversion for isobutane and propane is 100% for temperatures above 500°C.

In conditions of an excess of water vapor, it is possible to estimate the activation energy of the reforming of the alkane mixture components during the catalytic process in the annular microchannel on Rh- (La$_2$O$_3$, BaO)-Al$_2$O$_3$ catalysts. Following the work [6], taking into account the analogy of heat and mass transfer during laminar flow in the annular microchannel and its intensification at the input section, it is possible to calculate the mass-transfer coefficient for the this reactor. The diffusion coefficient for the components was calculated from [22]. The logarithm of the reaction rate constant in dependence of reverse temperature is showed for ethane and isobutane in figure 4. Lines correspond to approximation for ethane ($E_a = 72$ kJ/mol) and isobutane ($E_a = 59$ kJ/mol). The obtained values of activation energy of reforming on the tested catalyst for alkanes C$_2$-C$_4$ are less than for methane on Rh catalyst [6] and a mixture of methane and propane over Ni catalysts [13].

4. Summary

An experimental study of the steam conversion of mixture C$_2$-C$_4$ alkanes in an annular catalytic reactor in the temperature range 500-800°C for different contact times was carried out. It is shown that the greatest yield of hydrogen in the conversion of hydrocarbon gas is observed at a temperature above 550°C. It was estimated the activation energy of the reforming of the hydrocarbon gas mixture components in catalytic reaction.

![Figure 3](image_url)

Figure 3. Etane (a) and isobutane (b) conversion as a function of reaction temperature for contact time: 1-109, 2-82, 3–65 ms.
Figure 4. The logarithm of reaction rate constant versus inverse catalyst temperature. Symbols correspond to experiment for ethane (1) and for isobutane (2). Lines correspond to approximation for ethane (Ea = 72 kJ/mol) and isobutane (Ea = 59 kJ/mol).

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