Partial oxidation of light alkanes in microchannel

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Abstract. In this work, we conducted an experimental study of partial oxidation of fuel gas, consisting of a mixture of light C₁-C₄ alkanes, in an annular microreactor with a catalyst deposited on the inner wall of the channel with a carbon/oxygen ratio equal to one. The experiments were carried out at different contact times in the temperature range of the reactor of 450-750°C.

1. Introduction

Oxidative conversion is the most promising and energy-efficient method for processing hydrocarbon gases [1-3]. The resulting hydrogen/carbon monoxide ratio during partial oxidation is most convenient for producing liquid hydrocarbons (Fischer Tropsch synthesis). In contrast to steam reforming traditionally used in industry, in this case, synthesis gas is produced with minimum additional energy consumption. At the same time, other difficulties appear, since when using air as an oxidizing agent, it necessitates the separation of nitrogen from the reaction products. In the case of using oxygen as an oxidizing agent, it necessitates its expensive separation from nitrogen and ensuring process safety.

Also, an essential task of partial oxidation of C₂-C₄ alkanes is the creation of an effective and stable catalyst [1,3-5]. Depending on the ratio of the flow rates of hydrocarbon and oxygen, temperature, contact time, type of catalyst, and its carrier, a different composition of oxidation products can be obtained. In partial oxidation of C₁-C₄ alkanes, as well as for methane, platinum group metal catalysts are used. The first catalytic partial oxidation in reactors with a short contact time was performed in [4,5], then this process was studied in [6-12]. In these works, a high catalytic activity of the platinum group metals was shown. It was noted that rhodium is most effective for producing synthesis gas, and platinum is effective for producing olefins. The influence of catalyst support on this process was shown in [10].

Based on the experiments in the annular microchannel [12], the authors proposed the kinetics of partial oxidation for propane with a rhodium catalyst, similar to the previously proposed kinetics for partial oxidation of methane. Based on data [12], the authors of [13] presented their kinetics of catalytic reactions for partial oxidation of propane on an Rh / Al₂O₃ catalyst, including 62 reactions. In addition to catalytic reactions on the surface of the catalyst during partial oxidation of C₂-C₄ alkanes, homogeneous reactions in the reactor are significant, since the molecules of these hydrocarbons are less stable as compared to methane [2,14]. The kinetics of partial oxidation of ethane [2] included 490 elementary reactions, which corresponded well to the obtained experimental data. Due to the variety of possible options of the partial oxidation reactions of propane and butanes, their complete kinetics, including homogeneous reactions, have not yet been determined [4, 14]. As for partial oxidation of methane, an important question is as to how does partial oxidation occurs: whether through complete
combustion and subsequent steam reforming or direct oxidation of the alkane to form carbon monoxide and hydrogen. An analysis of the literature indicates that apparently, these reactions occur simultaneously only at different temperatures and catalysts; their influence is different.

The purpose of this work is to study experimentally the stability and efficiency of catalysts in a microchannel reactor during partial oxidation of fuel gas, consisting of a mixture of propane, butanes, ethane, and methane: to determine the composition of the reaction products at different temperatures and contact times, as well as the degree of conversion of feed gases and selectivity of the process products.

2. Experiment

2.1. Catalyst Preparation

Four types of catalysts were used in the work. The first catalyst for the partial oxidation of hydrocarbons had the following composition: 10 wt.% Rh / Ce0.4 Zr0.4 La0.2 Ox. The oxide phase, having a complex chemical composition, was prepared using the Pechini method: citric acid in a molar ratio to ethylene glycol of 1: 4 was dissolved in a small amount of water, added to ethylene glycol by heating in a water bath to 60°C, stirred to form a gel, and aqueous solutions of salts Ce (NO3) 3x6H2O, ZrO (NO3) 2x6H2O, La (NO3) 3x6H2O were added in the required quantities, stirred until uniform state, evaporated, dried with stirring to dryness, and calcined at 800°C for 2 hours. The active component (Rh) was applied by impregnation from an aqueous rhodium nitrate solution in a vacuum, producing heat treatment (drying at 120°C, calcinated at 600°C for 2 hours). An aqueous suspension was prepared from the catalyst and applied onto the treated metal rod by aerosol spraying.

The second catalyst consisted of two layers sequentially deposited on a metal rod: a steam reforming catalyst having a composition of 5% Rh / 3% La2O3 / 2% BaO / Al2O3 [15] and a catalyst for partial oxidation of hydrocarbons having a composition of 5% Rh / 20% La2O3 / 40% CeO2 / 40% ZrO2 in a mass ratio of 3:1. A sample with this catalyst showed the efficiency of oxidative steam reforming in previous work [16].

Two other catalysts were made on the basis of platinum on different supports: 10% Pt / 3% La2O3 / 2% BaO / Al2O3 and 10% Pt / CO2 / Al2O3. Before carrying out catalytic experiments, the catalyst was reduced directly in a catalytic reactor, feeding a mixture of 5 vol.% Н2 in nitrogen while heating to 500 °C at a rate of 5°C/min, and kept at this temperature for 2 hours.

2.2. Experimental Equipment

The experiments were performed using the setup described in [17, 18] for different flow rates of fuel, gas, and air. The mixture of fuel gas and air, set by the Bronkhorst mass controllers in the ratio C / O ≈ 1, was fed into the annular reactor with a gap of 950 μm. In the conducted experiments, preheating of the incoming gases was not carried out, and gas mixing took place near the reactor to exclude possible homogeneous reactions in the supply tubes. During the experiments, the temperature of the reactor was measured, as well as the volume and composition of reaction products using Agilent chromatographs with a mass selective detector, a Maestro with a thermal conductivity sensor. Unlike previous experiments on the catalytic conversion of hydrocarbons, the temperature of the reactor was measured both at the inlet and at the outlet of the reactor by K-type thermocouples [16-18]. By the ratio of the measured temperatures, it was possible to control the degree of isothermality of the reactor and the features of the thermal regime of partial oxidation of fuel gas. The temperature regime in the working area was maintained by an external electric heater [16-18].

3. Experimental Results

Figure 1 shows the measured concentrations of reaction products depending on the temperature of the reactor for a contact time t = 207 ms, where t = Vr / Qnu, Vr is the volume of the reactor, Qnu is the inlet gas flow rate under normal conditions (P = 101325 Pa, T = 273 K) on a two-layer catalyst. At the minimum tested flow rate, the values of the output concentrations are observed, which are
qualitatively close to the theoretically calculated values, presented in the graph by lines [19]. An analysis of the measured reactor temperatures showed the isothermality of the experiments at low gas flow rates. At high flow rates of inlet gases, there is a slight excess of the reactor inlet temperature over the outlet temperature at a temperature above 600 °C. This indicates that, in the beginning, some hydrocarbons are burned with the release of a large amount of heat, which is subsequently spent on the endothermic steam reforming reaction.

![Graph](image)

**Figure 1.** Concentrations of the output gases in partial oxidation of a mixture of hydrocarbon gases vs the temperature at a contact time of 207 ms on a two-layer catalyst. Lines correspond to equilibrium gas concentrations.

An important parameter of the reactions is the degree of conversion of the fuel gas components $X_i$ depending on the temperature and contact time $X_i = (n_{i,\text{in}} - n_{i,\text{out}}) / n_{i,\text{in}}$, where $n_i$ is the molar flow rate for each component. Figure 2 shows the degrees of conversion of fuel gas components with an average oxygen/carbon ratio of one, depending on the temperature of the reactor on a two-layer catalyst. Figure 3 shows the degrees of conversion of propane for different contact times obtained in our tests as well as the data on the degree of propane conversion from [8] for partial oxidation of propane for the same catalyst on foamed aluminosilicate (symbols 4). Points 5 correspond to the degree of propane conversion in the microchannel with a contact time of 12.7 ms. In contrast to our experiments, the carbon/oxygen ratio in [7, 8] was 0.8. Changes in the temperature at the inlet and outlet of the reactor in our experiments are similar to those in [7] on a microchannel reactor. The results on the degree of propane conversion are close to the data obtained during autothermal steam reforming for this catalyst [16]. Symbols 6 in Fig.3 show the propane conversion values for a contact time of 118 ms. As well as for steam and autothermal reforming of fuel gas, a decrease in the degree of conversion with a decrease in contact time is observed.
Figure 2. The degree of conversion of fuel gas components during its partial oxidation on a two-layer catalyst depending on temperature for a contact time of 207 ms.

![Graph showing conversion vs. temperature](image)

Figure 3. The degree of propane conversion during partial oxidation of fuel gas on a two-layer catalyst versus temperature for contact time: 1–207, 2–100, 3–79 ms. Points 4,5 correspond to the degree of propane conversion on the Rh catalyst obtained on foamed alumina [8], in the microchannel [7], respectively. Points 6 correspond to the data of autothermal conversion on the studied catalyst with a contact time of 118 ms.

![Graph showing propane conversion vs. temperature](image)

Figure 4 shows the ratio of the yield of moles of hydrogen to moles of fuel gas used versus temperature for one type of catalyst. Points 1-3 show the data of [16] with a fuel gas / air / water ratio of 1 / 4.5 / 7. Points 4-6 show the data for partial oxidation of fuel gas for the ratio of fuel gas / air of 1 / 7.2. The relative hydrogen yield in the case of autothermal reforming is more than twice higher than in the case of partial oxidation of fuel gas. The yield of hydrogen is determined by the reactor temperature for both oxidative steam reforming and partial oxidation of fuel gas. To carry out the oxidative steam conversion, water was additionally evaporated; water vapor with air was heated, and
the temperature of the reactor was maintained. During partial oxidation, the temperature of the reactor was maintained. At high flow rates, heating from the reaction maintained the temperature of the reactor.

**Figure 4.** Relative hydrogen yield during autothermal steam reforming and partial oxidation of fuel gas on a two-layer catalyst, depending on temperature. Points 1-3 correspond to autothermal steam reforming with a contact time of 118, 79.65 ms [16]. Points 4-6 correspond to partial oxidation of fuel gas with a contact time of 209, 100, 79 ms, respectively.

**Figure 5.** The degree of conversion of fuel gas components during its partial oxidation on a rhodium catalyst having mixed oxide support (Rh / Ce0.4 Zr0.4 La0.2 Ox) for a contact time of 198 ms.

Figure 5 shows the degrees of conversion of the fuel gas components on a rhodium catalyst in mixed oxide support. A similar change in the degree of conversion of the main components is observed, though with lower values. For platinum-based catalysts at the studied carbon/oxygen ratio,
the catalyst was deactivated, so that at a temperature of 700 for 3 hours the conversion of the studied mixture of hydrocarbons decreased significantly.

Conclusions
The catalytic partial oxidation of a mixture of light alkanes in a microchannel annular reactor at different temperatures and gas flow rates was experimentally studied for four types of catalysts. The studies showed the catalytic and stability efficiency of a two-layer rhodium catalyst, while the platinum catalyst on different carriers lost activity quickly. The obtained degree of propane conversion is compared with the corresponding data of other authors obtained in the process under study with the same type of catalyst used.

Acknowledgement
The study was performed in the framework of the state contract of IT SB RAS (AAAA-A17-117022850026-8).

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