Oxidative steam conversion of light alkanes

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Abstract. Oxidative steam reforming of C₂-C₄ alkanes was studied in an annular catalytic reactor under atmospheric pressure over two catalysts. Concentrations of the products of chemical reactions in the outlet gas mixture were measured at different temperatures of reactor. Effects of temperature have been compared for different residence time for the inlet gas ratio water/air/C₂-C₄ alkanes of 7:4.5:1.

1. Introduction

Steam, oxidative and dry (carbon dioxide) conversion of hydrocarbons (mainly methane) is the main way to produce hydrogen and synthesis gas [1,2]. Depending on the composition and flow rate of the inlet gas mixture, the properties and temperature of the catalyst, the products of steam, partial, oxidative steam reforming of hydrocarbons are determined. Due to the inevitable reduction in the volume of oil produced and the requirement to use associated petroleum gases (APG) [3,4], many studies have been performed on the conversion of light alkanes, the main components of APG: ethane, propane, butane [3-16]. The experiments were performed on microchannel reactors [7,8,16], pack [3,-6,11-13], foamed porous media [8], and special microlithic reactors [9].

The maximum yield of hydrogen occurs during the steam reforming of hydrocarbons, but it consumes a large amount of energy necessary for the evaporation of water and heating of steam. In oxidative reforming, the fuel gas is fed into the reactor along with oxygen (air) and steam, and thus the reactions of both partial oxidation and steam reforming occur simultaneously in the same reactor. Thermal neutrality can be achieved by adjusting the ratio of O₂ and H₂O in the feed stream, so that the net change in the reaction enthalpy is zero, avoiding the need for an external heat source after reaching the reaction temperature.

The theoretical ratio of the thermal neutrality of the oxidative steam reforming of lower alkanes was calculated in [11]. In addition, the rate of exothermic reactions is higher than endothermic reactions and they take place preferably at the inlet of reactor. On the other hand, endothermic reactions are based on heat transferred by convection and conductivity from the inlet side of the reactor. The conversion of the main components of the fuel gas (propane, butane) occurs at a lower temperature than methane conversion, so that both catalytic and homogeneous conversions of hydrocarbons occur simultaneously in the reactor [4]. When carrying out steam reforming of hydrocarbons, catalysts containing Ni or elements from the group of noble metals deposited on oxide systems are used. Nickel catalysts are promising for the reaction because of their low cost and high catalytic activity, but they are sensitive to carburization. Noble metal catalysts are characterized by high productivity, resistance to carbonization, high selectivity. Obtaining the complete kinetics of oxidative steam reforming of a mixture of alkanes for each catalyst is a difficult task; therefore,
obtaining experimental data for specific catalysts and creating “simplified kinetics” is a way to solve the problem.

In this work, a study of the oxidative steam reforming of hydrocarbon liquefied gas, consisting mainly of a mixture of ethane, propane and butane, was conducted in an annular microreactor coated with a rhodium catalyst on the inner wall of the channel. The degree of conversion of the various components of the starting product was determined depending on the temperature of the reactor and the contact time.

2. Experiment

2.1. Catalyst Preparation

Catalyst. When preparing the catalyst, its support — gamma-Al₂O₃ — was impregnated with solutions of lanthanum and barium nitrate salts, subjected to high-temperature calcination at 1050°C. Then being soaked with a solution of rhodium nitrate, it was calcined at 500°C. The metal rod was treated with acetone for degreasing, etched in 1M hydrochloric acid at 60°C. Then, a dense coating of titanium oxide from a complex organic solution was applied to prevent oxidation of the metal surface at high temperatures of the steam reforming process [16,19]. The procedure of aerosol deposition of the catalyst was repeated many times to achieve the required weight with two types of catalysts. The inner layer with rhodium nanoparticles on gamma alumina was contributed to steam reforming (5% Rh / 3% La₂O₃ / 2% BaO / Al₂O₃), the outer layer was sputtered over the first layer and accelerated the oxidation of hydrocarbons (5% Rh / 20% La₂O₃ / 40% CeO₂ / 40% ZrO₂). In order to avoid cracking of the deposited layers, the final calcination was performed at a rate of temperature rise of no more than 3°C/min. Before carrying out catalytic experiments, the catalyst was restored directly in the catalytic reactor, feeding a mixture of 5 vol.% H₂ in nitrogen while heated to 500°C at a rate of 5°C/min, and kept at this temperature for 2 hours. Figure 1 shows a picture of the outer layer catalyst obtained on a transmission electron microscope.

Figure 1. TEM picture of the catalyst.

2.2. Experimental Equipment

Experiments on the oxidative steam reforming of light hydrocarbons were carried out using the apparatus described in [17, 18] for three contact times of 65, 79, 118 ms with a water-to-air-fuel gas ratio of 7: 4.5: 1. This corresponded to the H₂O/C ratio = 2.3 and O₂/C = 0.9. A mixture of air, fuel gas and water, set by Bronkhorst gas controllers, was fed into the preheating chamber, where water
evaporation, preheating of air, water vapor and hydrocarbon gas occurred. The composition of the fuel gas was measured before each experiment. Then the gas mixture entered the annular reactor, where the catalytic reaction took place on the outer surface of the inner cylinder. To heat the reactor to the reaction temperature and stabilize 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. In the course of the experiments, the gas flow rates, reactor temperature, and the composition of the inlet and outlet gas mixtures were measured. The temperature of the reactor was measured with a K-type thermocouple. Analysis of the reaction products was performed using a Maestro gas chromatograph and gas chromatograph with an Agilent selective detector. The required temperature of the working area was created by the degree of heating of the external electric heater.

3. Experimental Results
Dry C2-C4 oxidative steam reforming products are represented in Figure 2 as a function of temperature for contact time of 79 ms. At the temperatures above 650°C, more than 45% of hydrogen is observed in these conversion products.

![Figure 2](image)

**Figure 2.** Concentrations of the output gases of the steam conversion of a mixture of hydrocarbon gases vs. the temperature at a contact time of 79 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 lines show the equilibrium concentrations of the reaction products, calculated using the Gas equation [20] program.

Figure 3 represents the degree of propane conversion $X_{Pr}$ vs. the temperature in an annular reactor at different flow rates of the inlet mixture under the conditions of excess water vapor $X_{Pr} = (n_{Pr,in} - n_{Pr,out}) / n_{Pr,in}$. A decrease in contact time leads to a decrease in hydrocarbon conversion. Increasing the number of carbon atoms in their steam reforming leads to more efficient reforming at the same temperature. Figure 4 shows the degree of conversion of butane vs. the temperature in an annular reactor. The degree of conversion of butane is greater than for propane and
to a lesser extent depends on the contact time. Calculated conversion for butane and propane is 100% for the temperatures above 500°C. For methane, calculated almost complete conversion is achieved at the temperatures above 800°C. The properties of the catalyst and the contact time affect the output composition of gases significantly.

![Figure 3](image1.png)

**Figure 3.** Propane conversion as a function of reaction temperature for contact time: 1 – 118, 2 – 79, 3 – 65 ms.

![Figure 4](image2.png)

**Figure 4.** Butane conversion as a function of reaction temperature for contact time: 1 – 118, 2 – 79, 3 – 65 ms.
Conclusion
An experimental study of oxidative steam conversion of the mixture of C₂-C₄ alkanes in an annular catalytic reactor in the temperature range of 500-800°C was carried out for different contact times. It is shown that the greatest yield of hydrogen at conversion of hydrocarbon gas is observed at the temperature above 650°C. Stability of a two-layer catalyst, whose inner layer is a catalyst for steam reforming of hydrocarbons (5% Rh / 3% La₂O₃ / 2% BaO / Al₂O₃), and the outer layer is a partial oxidation catalyst (5% Rh / 20% La₂O₃ / 40% CeO₂ / 40% ZrO₂) was shown. At the temperatures of 600-800°C, conversion is carried out in equilibrium for the contact times longer than 60 ms; for the shorter times there is deviation from the equilibrium with a lower output concentration of hydrogen.

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References
[1] Arutyunov V S, Krylov O V 1998 Oxidative Conversion of Methane (Nauka, Moskow)
[2] Holladay J D, Hu J, King D L and Wang Y 2009 Catalysis Today 139 244–60
[3] Usachev N Y, Charlamov V V, Belanova E P, Starostina T S and Krukovsky I M 2008 Russian Chemical Reviews 52 (4) 22–31
[4] Arutyunov V S, Savchenko V I, Sedov I V, Nikitin A V, Magomedov R N and Proshina A 2017 Russian Chemical Reviews 86 (1) 47–74
[5] Schadel B T, Duisberg M and Deutschmann O 2009 Catalysis Today 142 42–51
[6] Laosiripojana N and Assabumrungrat S 2006 Jour. of Power Sources 158 1348–57
[7] Silberova B, Venvik H J and Holmen A 2005 Catalysis Today 99 69–76
[8] Aartun I, Silberova B, Venvik H, Pfeifer P, Görke O, Schubert K and Holmen A 2005 Catalysis Today 110 469–78
[9] Junaedi C, Vilekar S, Walsh D, Mastanduno R, Morgan C and Roychoudhury S 2012 Jour of Hyd. Energy 37 10435–43
[10] Faria W L S, Dieguez L C and Schmal M 2008 App. Cat. B: Environ. 85 77–85
[11] Pino L, Vita A, Cipitì F, Lagana M and Recupero V 2006 Ap Cat A: Gen. 306 68–77
[12] Silva P P, Ferreira R A R, Noronha F B and Hori C E 2017 Catalysis Today 289 211–21
[13] Zhyryanova M M, Snytnikov P V, Shigarov A B, Belyaev V D, Kirillov V A and Sobyanin V A 2014 Fuel 135 76–82
[14] Faria E C, Rabelo-Neto R C, et al 2016 Catal. Lett. 146 2229–41
[15] Li Y, Wang X, Xie C, Song C 2009 Applied Catalysis A: General 357 213–22
[16] Dimov S V, Gasenko O A and Kuznetsov V V 2018 AIP Conf. Proceedings 1939 (1) 020008
[17] Kuznetsov V V, Vitovsky O V and Gasenko O A 2007 Therm. and Aeromech. 14 (2) 1–7
[18] Kuznetsov V V, Vitovsky O V and Gasenko O A 2009 Jour. of Eng. Thermo. 18 187–96
[19] Kuznetsov V V, Vitovsky O V, Gasenko O A 2015 Rus. Fed. Pat. № 2549619
[20] Morley C Gaseq chemical equilibrium program http://www.gaseq.co.uk