ISSN 0965-5441, Petroleum Chemistry, 2019, Vol. 59, No. 4, pp. 394–404. © Pleiades Publishing, Ltd., 2019.
Russian Text © L.P. Didenko, L.A. Sementsova, P.E. Chizhov, T.V. Dorofeeva, 2019, published in Neftekhimiya, 2019, Vol. 59, No. 3, pp. 271–281.

Steam Reforming of Methane and Its Mixtures with Propane in a Membrane Reactor with Industrial Nickel Catalyst and Palladium–Ruthenium Foil

L. P. Didenko[a, *], **L. A. Sementsova**[a], **P. E. Chizhov**[a], **and T. V. Dorofeeva**[a]
[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*
**e-mail: ludi@icp.ac.ru*

Received August 11, 2018; revised October 1, 2018; accepted December 10, 2018

Abstract—Steam reforming of methane and its mixtures containing 5 and 10% propane has been studied in a membrane reactor with an industrial nickel catalyst NIAP-03-01 and a membrane in the form of 30-μm foil made of a Pd–Ru alloy. At $T = 823$ K and a feed space velocity of 1800 h^{-1}, the almost complete methane conversion is achieved, the selectivity for CO_2 is more than 50%, and about 80% H_2 is recovered from the reaction mixture. High conversion of CH_4 in the membrane reactor under mild conditions allows the steam reforming of its mixtures with C_{2+} alkanes to be conducted in a single process, as shown by the example of model mixtures containing C_3H_8. Under selected conditions ($T = 773$ or 823 K, a feed space velocity of 1800 or 3600 h^{-1}, a steam/methane ratio of 3 or 5, atmospheric pressure), almost complete C_3H_8 conversion is observed. The main “undesirable” reaction is methanation, leading to a decrease in the CH_4 conversion. In the system under study, CH_4 is formed with an increase in the feed space velocity. Methanation occurs as a result of C_3H_8 hydrocracking at a steam/feedstock ratio = 3 or the hydrogenation of CO_2 as this ratio is increased to 5. The optimal conditions for steam reforming of methane mixtures containing up to 10% C_3H_8 are $T = 823$ K, steam/feedstock ratio = 5, and the feed space velocity of 1800 h^{-1}. Under these conditions involving evacuation of the permeate, the feedstock conversion is complete, the selectivity for CO_2 is 50%, and more than 70% H_2 is recovered from the reaction mixture.

Keywords: steam reforming, methane/propane mixtures, membrane reactor
DOI: 10.1134/S0965544119040054

INTRODUCTION

Hydrogen is the most promising clean energy source derived from natural raw materials. Due to the rapid development of hydrogen power engineering, the demand for these raw materials is increasing. The need for high-purity hydrogen is especially great, as, for example, it is used for low-temperature fuel cells with polymeric proton-exchange membranes, where the CO concentration should not exceed 10 ppm [1]. The main industrial method for producing H_2 is steam reforming of methane on nickel catalysts, in which the following reactions occur simultaneously:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206 \text{ kJ/mol}, \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ/mol}, \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^0_{298} = 165 \text{ kJ/mol}. \tag{3}$$

A typical industrial process for H_2 production includes the high-temperature step of steam reforming of feedstock (1) followed by two steps of steam reforming of CO by water-gas shift reaction (2) proceeding at a lower temperature and the subsequent step of H_2 purification, which in most cases is carried out using the pressure swing adsorption technique. The yield of the products is limited by thermodynamic equilibrium and, due to the high endothermicity of reactions (1) and (3), temperatures above 973 K are required to achieve high methane conversion. For example, the methane conversion higher than 80% can be obtained at temperatures above 1123 K. In steam reforming, natural gas is used as feedstock that contains 3–7 vol % C_{2+} hydrocarbons in addition to methane. A particular composition of natural gas depends on the gas field. For example, natural gas of the Urengoy field in Russia has the following composition, %: methane, 87; ethane, 6.2; propane, 3.4; butane, 1.98; pentane, 0.76; carbon dioxide, 0.12; and nitrogen, 1.1 [2]. In addition to natural gas, associated petroleum gases (APG) containing on average, %: 50–70 CH_4, 5–10 C_2H_6, 5–15 C_{3+}, 1–10 N_2, and 1–10 CO_2 can be used as hydrocarbon feedstock. However, this valuable feedstock is used extremely inefficiently. In Russia, about 15.7 billion m^3/year of APG is flared, which is about 24% of its total amount and causes significant environmental damage [3]. The steam reforming of a methane mixture with C_{2+} hydrocarbons in a single process is impossible, since catalyst-deactivating carbon deposits are rapidly formed from methane homologues at high temperatures. The rate of this reaction increases with temperature and with an increase in the number of carbon atoms in a C_{2+} hydrocarbon. In this regard, it is necessary to remove C_{2+} hydrocarbons from the feedstock. In the industrial process, for this purpose, a pre-reforming stage is used, consisting in the steam conversion of methane homologues on nickel catalysts at temperatures of 673–773 K to yield a mixture of methane, hydrogen, and carbon oxides [4, 5]. To prevent the formation of carbon deposits, pre-reforming is carried out at a steam to methane ratio of 2.5–4. The process involves the following irreversible reactions of steam reforming of methane homologues (C_nH_m, $n \geq 2$):

$$C_nH_m + nH_2O \rightarrow nCO + (m/2 + n)H_2 \quad \Delta H^0_{298} > 0, \tag{4}$$

$$C_nH_m + 2nH_2O \rightarrow nCO_2 + (m/2 + 2n)H_2 \quad \Delta H^0_{298} > 0. \tag{5}$$

These reactions are accompanied by the water-gas shift reaction and reversible exothermic methanation reactions:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^0_{298} = -205.9\ \text{kJ/mol}, \tag{6}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H^0_{298} = -164.7\ \text{kJ/mol}, \tag{7}$$

$$C_nH_m + (2n - m/2)H_2 \rightarrow nCH_4 \quad \Delta H^0_{298} < 0. \tag{8}$$

The pre-reforming reaction can be used to produce H_2, and this possibility is being actively investigated [6–9]. It was shown that the temperature and steam/hydrocarbon ratio affect in similar ways the conversion of ethane, propane, and butane on a rhodium catalyst and the product selectivity [9]. The conversion of a mixture containing 86.7% CH_4, 8.1% C_2H_6, 2.0% C_3H_8, and 0.4% C_4H_{10} occurs in two temperature regions: ethane, propane, and butane are almost completely consumed to give a mixture of H_2 and carbon oxides below 673–723 K, and the conversion of CH_4 occurs with a further increase in temperature [9]. In principle, in order to conduct steam reforming of a mixture of methane and its closest homologues in a single process, it is necessary to lower the methane conversion temperature. For this purpose, membrane technology can be used, combining the reaction process and H_2 removal through the membrane. As a result, the equilibrium of the thermodynamically controlled reaction of steam reforming of methane is displaced, thereby making it possible to achieve a high conversion at lower temperatures. In addition to lowering the reaction temperature, the simultaneous conversion of CH_4 and its closest homologues in the membrane reactor eliminates some steps of the conventional steam reforming process of natural gas, such as pre-reforming, additional oxidation of CO by water-gas shift reaction, and fine H_2 purification from CO. In general, this will greatly simplify the process flowchart and reduce energy costs. This demanding problem is the subject matter of this study.

The data presented in the literature show that in a membrane reactor, it is possible to achieve high methane conversion at temperatures of 723–873 K [10–12]. A nickel catalyst is most frequently used in the reaction because of its high activity, availability, and low cost. Not only Ni, but also Ru, Rh, Ir, and Pt are active in the reaction. Palladium alloys are the most promising as a hydrogen-selective membrane material due to the unique properties of palladium, such as are the catalytic surface, on which H_2 molecules dissociate into atoms diffusing at a high rate in the metal lattice, and the ability of palladium to absorb a large volume of hydrogen exceeding 600 times its own volume. To obtain high-purity hydrogen, dense palladium membranes (foils) with 100% hydrogen selectivity are the most suitable. They are inferior to composite palladium membranes in hydrogen permeability because of a greater thickness, but have significant advantages, such as ease of fabrication, ease of connection with the structural elements of the membrane module, and ease of regeneration. The performance of palladium foil can be enhanced by alloying Pd with some additives that increase the H_2 permeability, for example, 93% Pd–7% Y, 60% Pd–40% Cu, 94% Pd–6% Ru, and 93.5% Pd–6% In–0.5% Ru [13, 14]. Preparing a thin (down to 7 μm) dense foil from such alloys by magnetron sputtering will make it possible to achieve a further increase in hydrogen permeability [15–17].

The feasibility of steam reforming of CH_4 mixtures with C_{2+} homologues in a membrane reactor was shown by Shirasaki et al. [18]. They presented a membrane reformer for producing high-purity hydrogen by steam reforming of natural gas at temperatures of 768–813 K. Natural gas of a constant composition containing 88.5% CH_4, 4.6% C_2H_6, 5.4% C_3H_8, and 1.5% C_4H_{10} was used in their study, but the effect of change in the feedstock composition on the parameters of the membrane process was not investigated. However, the C_{2+} content in the feedstock may vary depending on the gas field and thus can affect the feedstock conversion and the selectivity for steam reforming products in the membrane reactor.

In this study, methane mixtures containing 5 and 10% C_3H_8 were taken as models. The steam conversion of the mixtures was investigated by varying the temperature, the feed space velocity, and the steam/methane ratio.

The aim of the work was to optimize the conditions of the membrane process to obtain the maximum conversion in the reaction of steam reforming of methane mixtures with propane.

EXPERIMENTAL

Membrane Reactor

A foil with a thickness of 30 μm made of Pd–6% Ru alloy was kindly provided by staff members of Laboratory No. 12 at the Institute of Metallurgy and Materials Science of the Russian Academy of Sciences (IMET RAS, Moscow). Foil blanks were melted in an electric arc furnace in an inert atmosphere. A foil of a given thickness was obtained by cold rolling with intermediate vacuum annealing. The foil membrane had a disk shape with a diameter of 56 mm (effective surface area of 15.2 cm^2). To maintain mechanical strength, it was sandwiched between stainless steel fine mesh sheets. The membrane reactor had a feed (retentate) compartment and an H_2 withdrawal (permeate) compartment separated by the membrane. The design of the reactor is detailed in [19]. In the retentate compartment, atmospheric pressure was maintained. The driving force for the withdrawal of H_2 from the reaction mixture through the membrane was created by reducing the partial pressure of H_2 in the permeate compartment. For this purpose, nitrogen as the sweep gas was fed to the permeate compartment countercurrently to the feedstock at a preset flow rate (150 cm^3/min). In some experiments, vacuum pumping was used to extract H_2 from the permeate compartment.

Steam Reforming of Hydrocarbon Feedstock

The feedstock used was either 100% CH_4 or its mixtures containing 5 and 10 vol % C_3H_8. The retentate compartment was charged with 2 cm^3 (3.35 g) of the NIAP-03-01 industrial nickel catalyst for steam reforming of natural gas (manufactured by NIAP-KATALIZATOR, Novomoskovsk). The feedstock was mixed with steam in the required ratio and fed at a given rate to the catalyst through holes located around the periphery of the retentate compartment, and the resulting products were withdrawn through the central hole and passed through a condenser to condense unreacted water. The volumetric flow rate of “dry” gases containing H_2, CO, CO_2, and unreacted CH_4 was measured at the reactor outlet using a soap bubble flow meter, and the gas was fed to a chromatograph. The product composition was determined on-line using a Kristall-5000 chromatograph with flame ionization and thermal conductivity detectors. The H_2 content in the products was determined on a column with molecular sieves 13X (2 mm × 2 m, 50°C, carrier gas argon). The hydrocarbon composition of the products was determined on a HP-Al/KCl column (0.5 mm × 30 m, 80°C, carrier gas helium). The concentrations of CO and CO_2 were determined on a column packed with activated carbon (2 mm × 2 m, 100°C, carrier gas helium). The concentrations of the products were calculated using the method of absolute calibration.

Gas flow rates were controlled with RRG-12 gas flow regulators (Eltochpribor, Zelenograd). The reactor was heated by an electric oven. The temperature in the reactor and in the furnace was monitored with the use of chromel–alumel thermocouples.

The methane conversion (α, %), the product selectivity (*S*, %) and the H_2 recovery through the membrane (φ, %) were calculated by the equations:

$$\alpha = \frac{V^{\text{in}} X^{\text{in}}_{\text{CH}_4} - V^{\text{out}} X^{\text{out}}_{\text{CH}_4}}{V^{\text{in}} X^{\text{in}}_{\text{CH}_4}} \times 100\%,$$

$$S_{\text{prod}} = \frac{X^{\text{out}}_{\text{prod}}}{X^{\text{out}}_{\text{H}_2} + X^{\text{out}}_{\text{CO}} + X^{\text{out}}_{\text{CO}_2} + X^{\text{out}}_{\text{CH}_4}} \times 100\%,$$

$$\varphi = \frac{V^{\text{perm}} X^{\text{perm}}_{\text{H}_2}}{V^{\text{perm}} X^{\text{perm}}_{\text{H}_2} + V^{\text{ret}} X^{\text{ret}}_{\text{H}_2}} \times 100\%,$$

where V^{in} is the flow rate of the gas stream at the reactor inlet, cm^3/min; $X^{\text{in}}_{\text{CH}_4}$ is the volume concentration of CH_4 in the gas stream at the reactor inlet, %; $X^{\text{out}}_{\text{CH}_4}$ is the volume concentration of methane in the products at the reactor outlet, %; $V^{\text{out}}_{\text{prod}}$ is the flow rate of products at the reactor outlet, cm^3/min; and X_{out} is the volume concentration of the product in the mixture leaving the reactor, %;

The catalyst used in the form of grains of 0.2–0.4 mm was pretreated directly in the reactor with a (60% H_2–40% Ar)–steam mixture for 60 min at the temperature of the experiment (preliminary experiments showed that a change in the catalyst pretreatment temperature in the range of 773 –973 K does not affect its activity).

RESULTS AND DISCUSSION

Experiments with 100% Methane

Initially, experiments were performed in the absence of C_3H_8. Their goal was to determine reaction conditions that allow the temperature to be kept as low as possible while maintaining high rates of methane conversion in the membrane reactor. The effect of H_2 recovery through the membrane on the methane conversion and the product selectivity was revealed on the basis of comparison with experiments without H_2 removal ("nonmembrane" reaction), in which a gastight stainless steel partition was installed instead of the membrane. In the majority of studies reported in the literature, an increased pressure is used in the retentate compartment of membrane reactor. Despite the adverse effect on the position of thermodynamic equilibrium of the reaction under study, an increase in pressure allows an increase in the H_2 flux through the membrane, which generally has a positive effect on the feedstock conversion. However, atmospheric pressure is more preferable as far as the use of steam reforming of hydrocarbon feedstock in small-scale units with fuel cells for generating electricity is concerned, where the use of high-pressure compressor units is problematic [20]. Thus, the reaction was investigated at atmospheric pressure in this work.

Effect of temperature. The effect of temperature on the methane conversion and the selectivity for CO at a feed space velocity of 3600 h^{-1} and a steam/methane ratio of 3 is illustrated in Fig. 1a. It can be seen that with an increase in temperature, the conversion of CH_4 and the CO selectivity increase (curves *1*, *4*), exceeding their values for the "nonmembrane" reaction represented by curves *2* and *5*, respectively. These relationships reflect the favorable effect of temperature on both endothermic reaction (1) and the flux of H_2 through the membrane. Compared with the experiments without H_2 withdrawal, the methane conversion at 973 K is increased by 15.5%. The increase in conversion relative to the "nonmembrane" value becomes smaller with a decrease in temperature, and it does not exist at all at 773 K. This may be due to a decrease in the H_2 uptake through the membrane with decreasing temperature. For example, it is 64–68% at 923–973 K and 57% at 773 K (Fig. 1b, curve *1*). The reason for the lower recovery of H_2 may be a decrease in its partial pressure in the reaction mixture with a decrease in temperature. It is possible to increase the withdrawal of H_2 by pumping it out of the permeate section using a vacuum pump, which can reduce the H_2 pressure in the permeate to 3 mmHg. It can be seen that during evacuation, the withdrawal of H_2 increases to 79–80% in the interval of 923–973 K, and it is 70% at 773 K (Fig. 1b, curve *2*). Due to an increase in the H_2 removal, the methane conversion increases to 100%, in the temperature range of 923–973 K and to 38% at 773 K (Fig. 1a, curve *3*).

These results reflect the peculiarity of the membrane process, in which the condition for maximizing the conversion in a membrane reactor is close values of the rates of formation of H_2 and its removal through the membrane, a fact that has been experimentally shown in many papers, for example [21–24]. Apparently, in the system under study using the sweep gas, this balance of rates is not reached, the imbalance being most pronounced at 773 K, at which an increase in the methane conversion relative to the "nonmembrane" value is not observed at all (Fig. 1a, curves *1*, *2*). In the experiments with permeate evacuation, the rate of H_2 withdrawal from the reaction mixture increases, thereby leading to an increase in methane conversion over the entire temperature range. The selectivity for CO is higher than the "nonmembrane" value, and this difference increases with an increase in temperature (Fig. 1a, curves *4*, *5*), which is explained by a decrease in CO consumption in exothermic water-gas shift reaction (2). When the permeate is subjected to vacuum pumping, the CO_2 selectivity increases and the concentration of CO significantly decreases (Fig. 1a, curve *6*) by its consumption in the water-gas shift reaction.

Effect of feed space velocity. The effect of the space velocity of the methane–steam mixture on the methane conversion and the selectivity for CO and CO_2 at 823 K and a steam/methane ratio = 3 is shown in Fig. 2a. It can be seen that the methane conversion increases with a decrease in the feed space velocity from 8.0% at 9600 h^{-1} to 78% at 1800 h^{-1} (curve *1*). This is due to the increase in both the time of contact of feedstock with the catalyst and the H_2 recovery from 40% at 9600 h^{-1} to 70% at 1800 h^{-1}.

The selectivity for CO_2 increases from 7% at 9600 h^{-1} to 34% at 1800 h^{-1} (curve *2*). In this case, the selectivity for CO varies only slightly, in the range of 7.1–6.2% (curve *3*). With an increase in the removal of H_2 by evacuating the permeate, the selectivity for CO_2 increases to 50% at 1800 h^{-1}, and the conversion of methane increases to 100% (shown by arrows in curves *1* and *2*). Carbon dioxide is formed as a result of consumption of CO, the selectivity for which decreases (shown by the arrow in curve *3*). These data show that the selectivity of the formation of CO_2 by water-gas shift reaction (2) is significantly affected by an increase in the rate of H_2 removal through the membrane. Even with an increase in temperature to 973 K, which is unfavorable for exothermic reaction (2), at low feed space velocities of 1800 and 3600 h^{-1}, evacuation of the permeate leads to a decrease in selectivity for CO due to its consumption for the formation of CO_2 (Fig. 3).

Effect of steam/methane ratio. The methane steam reforming reaction is usually carried out at a steam/methane ratio exceeding the stoichiometric ratio. First, this is necessary for increasing the conversion of CH_4 and, second, for preventing the formation of carbon deposits. The possibility of using a lower

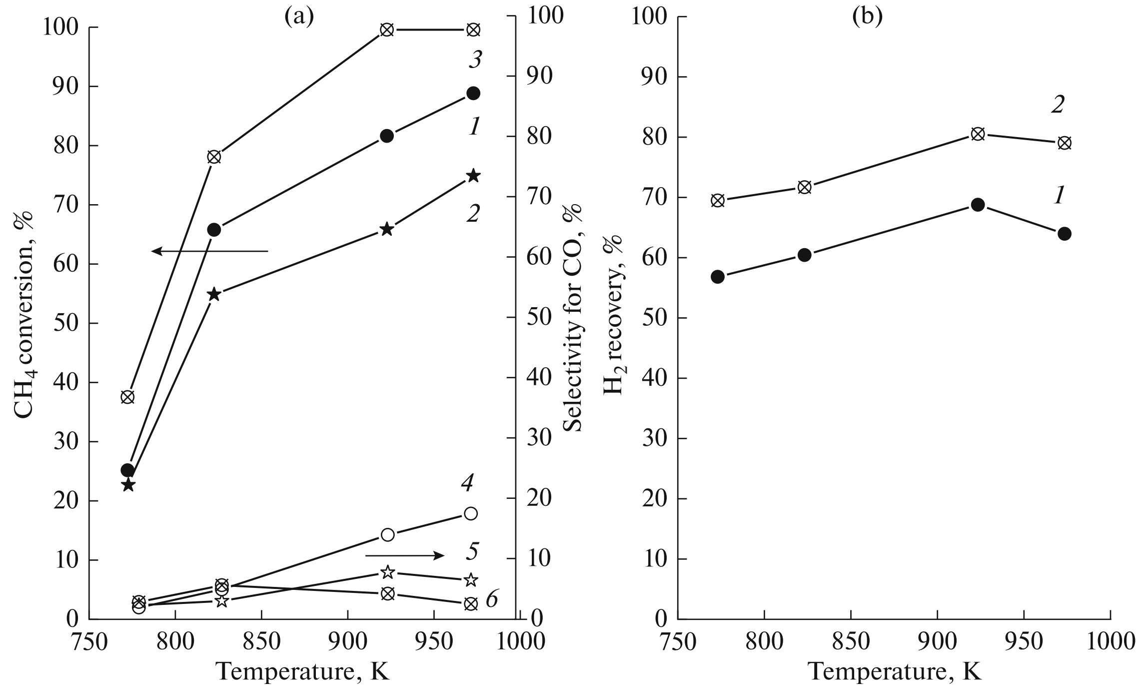

Fig. 1. (a) Temperature dependence of (*1*–*3*) methane conversion and (*4*–*6*) CO selectivity at a feed space velocity of 3600 h^{-1} and steam/methane = 3 (*1*, *4*) with H_2 withdrawal (sweep-gas flow rate 150 cm^3/min), (*2*, *5*) without H_2 withdrawal, and (*3*, *6*) with permeate evacuation used instead of sweep gas. (b) Influence of temperature on the H_2 recovery through the membrane using (*1*) sweep gas and (*2*) permeate evacuation.

temperature in the membrane reactor makes it possible to significantly reduce the yield of carbon deposits, so that a lower steam/methane ratio can be used. However, a higher ratio is required to increase the selectivity for CO_2. Therefore, there is an optimum of 2.0–4.0, which is commonly used in the membrane process. The effect of the steam/methane ratio on the methane conversion and the selectivity for carbon oxides in the membrane reactor at $T = 823$ K and a space velocity of the methane–steam mixture of 3600 h^{-1} is shown in Fig. 2b. It can be seen that with an increase in the ratio from 2 to 5, the methane conversion increases from 45 to 80% (curve *1*), the selectivity for CO decreases slightly from 5.0 to 4.7% (curve 3), and the selectivity for CO_2 increases from 20 to 40% (curve *2*). Despite the fact that the reaction mixture is dilute and the partial pressure of H_2 decreases with an increase in the steam excess, the increasing methane conversion compensates for the negative effect of dilution and, therefore, the H_2 recovery generally increases from 45% at a ratio of 2–3 to 50% at a ratio of 4–5.

In general, the results presented above show that under the mild conditions (atmospheric pressure and 823 K) in the membrane reactor, an 80% methane conversion can be achieved at methane–steam space velocities of 1800–3600 h^{-1} in the catalytic system under investigation. An increase in the H_2 flux through the membrane during the evacuation of permeate leads to the almost complete conversion of CH_4 and a CO_2 selectivity of about 50%. In connection with this, the mixtures of methane with propane were studied at temperatures of 773 and 823 K, space velocities of 1800 and 3600 h^{-1}, and steam/feedstock ratios of 3 and 5.

Experiments with Mixtures of Methane and Propane

The steam reforming of C_{2+} alkanes, as well as their mixtures with methane, was studied predominantly in the “nonmembrane” reactions. The alkane conversion and the product selectivity are mainly affected by the temperature and steam/feed ratio. At a low ratio (0.39–0.58) in the temperature range of 423–598 K, along with alkane steam reforming, reactions (6) and (7) occur, leading to the formation of CH_4 [25]. During the conversion of a mixture containing 17 vol % C_3H_8, 34 vol % CH_4, and 49 vol % H_2O, both the steam reforming of propane and hydrocracking according to reaction (8) occur on the nickel catalyst NIAP-18 in the temperature range of 523–723 K, leading to an increase in the CH_4 content, with the selectivity for CH_4 increasing with decreasing temperature [26]. The complete conversion of C_{2+} alkanes

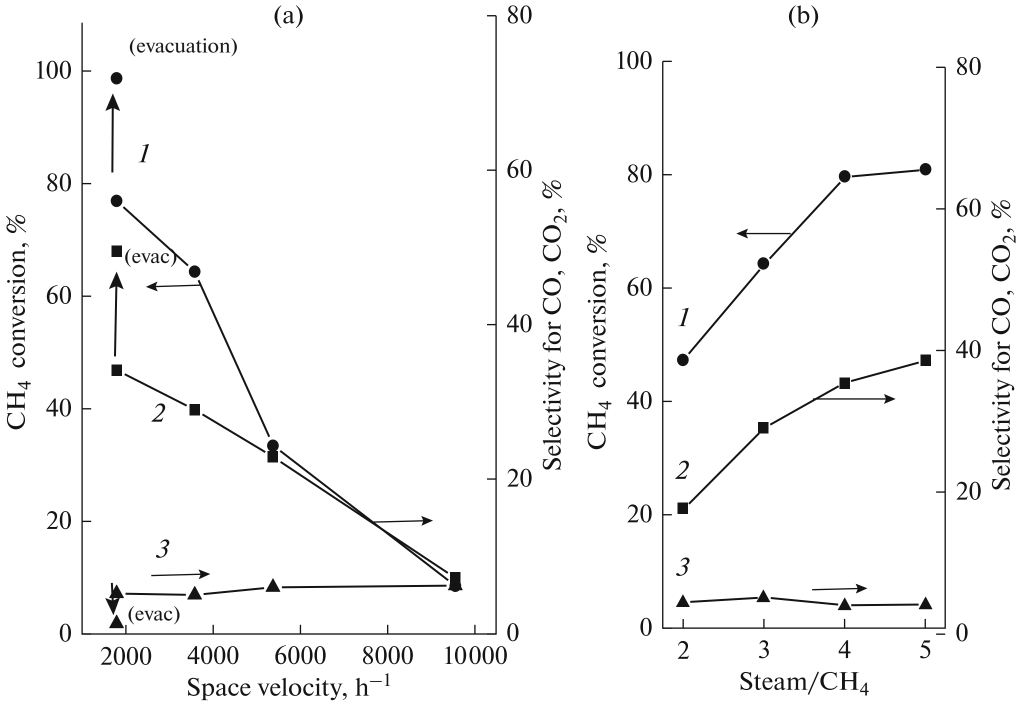

Fig. 2. Dependence of (*1*) methane conversion and selectivity for (*2*) CO_2 and (*3*) CO on (a) the feed space velocity at a steam/methane ratio of 3 and (b) the steam/methane ratio at a space velocity of 3600 h^{-1}. $T = 823$ K.

in the reaction with steam is observed in the temperature range of 723–773 K; that is, the reaction is almost irreversible. However, simultaneously with steam reforming, the hydrogenation reactions of carbon oxides occur to give CH_4; these reactions are limited by thermodynamic equilibrium, which impedes the achievement of high conversion of a C_{2+} alkane. Therefore, it is reasonable to carry out these reactions in a membrane reactor, where the removal of H_2 through the membrane reduces the contribution of these reactions and, thus, increases the alkane conversion and the yield of H_2. This suggestion was confirmed by Rarib et al. [28], who studied the steam reforming of propane in a fluidized bed membrane reactor using the Haldor Topsoe nickel-containing industrial catalyst RR-212 and a membrane in the form of $Pd_{77}Ag_{23}$-alloy foil at temperatures of 723–823 K and showed a significant increase in propane conversion compared with the "nonmembrane" reaction. The reaction was investigated at a low feed flow rate, which was 0.595 mL/min, and a temperature of 798 K. Under these conditions, the yield of H_2 was 9.26 moles, which is close to the theoretically possible maximum of 10 moles per mole of propane. However, during the study, the H_2 selectivity of the membrane decreased due to the appearance of defects. In this work, we studied the steam reforming of methane mixtures with propane in the membrane reactor at significantly higher feed space velocities of 1800 and 3600 h^{-1} and temperatures of 773 and 823 K, selected as a result of the above-described experiments with 100% CH_4. Tables 1 and 2 present the results of the study of the mixtures containing 5 and 10% C_3H_8 at steam/feedstock ratios of 3 and 5, respectively. To remove H_2 from the reaction mixture through the membrane, both sweep gas and permeate evacuation were used. It can be seen that the C_3H_8 conversion was complete under all the conditions.

As shown above in the general form for C_nH_m alkanes, their interaction with steam can occur via reactions (4)–(8). Using the example of the "nonmembrane" reaction of steam reforming of a methane mixture containing 17% C_3H_8 and 49% H_2O in the temperature range of 523–753 K, it was shown that depending on temperature, C_3H_8 is converted by the following reactions [26]:

at temperatures less than 623 K:

$$C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2, \qquad (5a)$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4, \qquad (8a)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (7a)$$

at temperatures above 623 K, C_3H_8 steam reforming predominantly yields CO, which subsequently enters into reactions with H_2 and H_2O:

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2, \qquad (4a)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O, \qquad (6a)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2. \qquad (2a)$$

It can be seen that the propane transformation scheme includes methanation reactions (6a), (7a), and (8a) along with steam reforming reactions (4a) and (5a). The formation of methane is undesirable because it reduces the conversion parameter. In this context, the analysis of the data included in Tables 1 and 2 has focused on determining the conditions under which these undesirable reactions may occur. The effect of C_3H_8 was established by comparing the data for the mixtures and 100% CH_4 under the same conditions. The data presented in Table 1 show that with the steam/feedstock ratio of 3, an increase in the CH_4 content of the products is observed only at $T =$ 823 K and the feed space velocity of 3600 h^{-1}, and this leads to a decrease in methane conversion from 64.4% for 100% CH_4 to 56.8% for its mixture containing 10% C_3H_8. An increase in the rate of H_2 removal from the reaction products by evacuating the permeate does not have a noticeable effect on the methane conversion, and the selectivities for CO and CO_2 also change little. These data suggest that the formation of CH_4 leads to irreversible reaction (8a). Apparently, as a result of a decrease in the time of feedstock contact with the catalyst with an increase in the feed space velocity, the conversion of C_3H_8 occurs not only by the reaction of steam reforming, but also by the hydrocracking reaction. With a decrease in space velocity to 1800 h^{-1}, C_3H_8 hydrocracking is not observed and methane and propane are converted by the steam reforming and water-gas shift reactions, as indicated by closeness of product compositions and conversion values. The results of similar studies at the steam/feedstock ratio of 5 (see Table 2) that both at 773 and 823 K, products also have a higher CH_4 content at the higher feed space velocity of 3600 h^{-1}. As a result, the conversion of CH_4 from mixtures with C_3H_8 is lower than in the absence of C_3H_8 to be 46.9% at $T =$ 773 K and 62.9% at 823 K.

In the case of permeate evacuation, the values of these parameters increase significantly and the CO_2 selectivity also increases. The effect of the increase in the H_2 withdrawal rate, which is observed when the permeate is evacuated, on the methane conversion indicates the reversible nature of a reaction by which methane can be produced. This reaction can be reversible reaction (7a) of CO_2 hydrogenation. This assumption is supported by an increase in CO_2 selectivity with increasing methane conversion. At a space velocity of 1800 h^{-1}, the product compositions and the conversions of methane and its mixtures with C_3H_8 are close; that is, the formation of CH_4 does not occur. The almost complete conversion of CH_4 from a mixture containing 10% C_3H_8 was attained by evacuating the permeate at 823 K and a space velocity of 1800 h^{-1}. Under these conditions, the selectivity for CO_2 is 53% and more than 70% of H_2 is removed from the mixture.

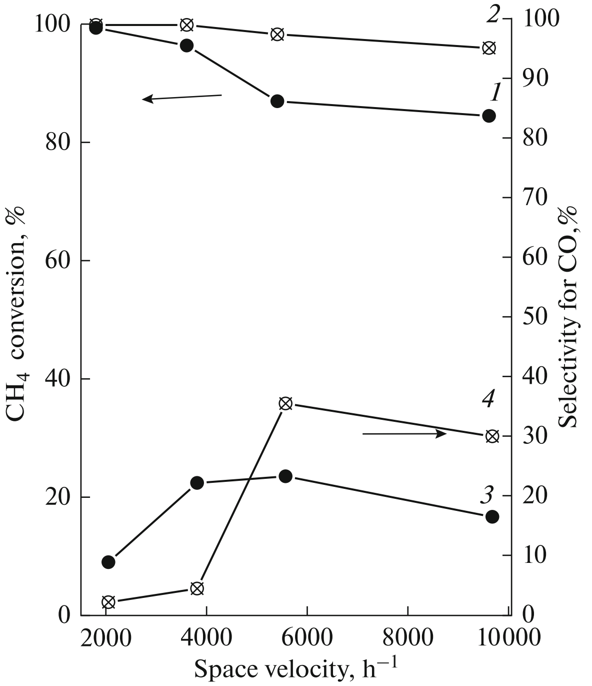

Fig. 3. Influence of feed space velocity on (*1*, *2*) methane conversion and (*3*, *4*) CO selectivity at $T =$ 973 K and a steam/methane ratio of 3 in experiments with (*1*, *3*) sweep gas and (*2*, *4*) permeate evacuation.

Catalyst and Membrane Stabilities

Catalytic reactions of conversion of alkanes are complicated by the formation of carbon deposits. In a membrane reactor, their yield generally increases, with the increase being due to a decrease in the stabilizing effect of H_2 as its content in the reaction mixture decreases. Carbon deposits can accumulate in the catalyst bed, resulting in catalyst deactivation. In addition, as a result of the buildup of carbon deposits on the surface of the membrane, its hydrogen permeability may decrease and defects may appear, leading to a decrease in H_2 permselectivity. The stability of the given catalytic system in the membrane reactor was studied using a methane mixture containing 5% C_3H_8 as feedstock at $T =$ 823 K, a space velocity of 3600 h^{-1}, and a steam/feedstock ratio of 3. The sweep gas was used to remove H_2. It was found that within 50 h, the methane conversion varied within 60–62% and the selectivites for CO and CO_2 were 7.0– 8.5 and 21–

Table 1. Parameters of steam reforming of methane and its mixtures with propane at a steam/feed ratio of 3

Mixture	Content in retentate, % (on dry residue basis)				Conversion, %			Selectivity, %				H_2 recovery, %	
	CH_4	CO	CO_2	H_2	CH_4		C_3H_8	CO		CO_2			
					sweep gas	evacuation	sweep gas	sweep gas	evacuation	sweep gas	evacuation	sweep gas	evacuation
$T = 773$ K, feed space velocity 3600 h^{-1}													
100% CH_4	38.0	2.2	24.5	37.6	27.4	37.6	–	2.1	5.1	24.0	30.0	57.8	68.1
+ 5% C_3H_8	40.9	2.6	22.3	35.0	30.9	65.7	99.8	2.5	1.9	21.5	34.6	61.0	68.1
+ 10% C_3H_8	39.1	4.0	20.4	36.0	34.8	68.2	100	4.0	2.5	21.3	32.5	65.2	61.7
$T = 773$ K, feed space velocity 1800 h^{-1}													
100% CH_4	18.2	3.2	30.7	50.3	43.6	80.8	–	2.8	1.0	28.7	43.2	59.4	78.9
+ 5% C_3H_8	14.2	2.6	32.1	51.5	58.4	74.8	99.9	2.4	3.0	30.0	47.0	54.6	76.8
+ 10% C_3H_8	18.4	2.5	34.2	44.6	63.2	91.4	99.8	2.5	1.1	34.3	51.4	69.3	77.6
$T = 823$ K, feed space velocity 3600 h^{-1}													
100% CH_4	16.4	6.9	26.3	51.8	64.4	78.4	–	6.2	11.0	23.6	44.0	51.9	73.6
+ 5% C_3H_8	20.0	7.9	25.6	47.8	60.7	92.4	99.3	7.5	2.7	22.7	40.2	65.9	77.3
+ 10% C_3H_8	26.0	8.4	22.0	44.8	56.8	60.8	99.9	8.0	9.9	20.8	26.3	62.8	73.7
$T = 823$ K, feed space velocity 1800 h^{-1}													
100% CH_4	6.9	5.5	35.0	52.8	77.2	98.8	–	5.3	1.4	34.3	49.8	54.4	76.9
+ 5% C_3H_8	5.7	4.8	36.4	53.1	84.0	97.5	100	4.7	2.8	35.8	57.9	62.1	75.1
+ 10% C_3H_8	7.5	5.3	34.9	52.0	80.2	–	100	5.4	–	36.2	–	64.1	–

Table 2. Parameters of steam reforming of methane and its mixtures with propane at a steam/feed ratio of 5

Mixture	Content in retentate, % (on dry residue basis)				Conversion, %			Selectivity, %				H_2 recovery, %	
	CH_4	CO	CO_2	H_2	CH_4		C_3H_8	CO		CO_2			
					sweep gas	evacuation	sweep gas	sweep gas	evacuation	sweep gas	evacuation	sweep gas	evacuation
T = 773 K, feed space velocity 3600 h^{-1}													
100% CH_4	12.0	1.3	26.5	58.8	60.5	–	–	1.4	–	29	–	42.3	
+ 5% C_3H_8	14.7	2.5	26.0	55.9	59.7	75.1	99.7	2.4	2.4	28.1	39.8	63.7	68.4
+ 10% C_3H_8	16.1	2.4	27.7	54.9	46.9	71.9	98.7	2.2	2.2	26.1	50.2	50.3	68.8
T = 773 K, feed space velocity 1800 h^{-1}													
100% CH_4	4.4	1.6	36.0	57.1	93.5	95.8	–	1.8	2.7	40.0	53.6	78.9	82.5
+ 5% C_3H_8	4.1	1.3	33.3	61.5	91.5	86.0	99.8	1.3	0.8	33.3	53.0	69.1	69.8
+ 10% C_3H_8	5.7	1.7	39.5	53.0	84.4	97.6	100	1.8	1.2	36.0	57.0	63.3	79.9
T = 823 K, feed space velocity 3600 1800 h^{-1}													
100% CH_4	5.6	3.8	29.0	60.6	82.7	96.6	–	4.0	1.4	28.0	43.1	59.3	68.4
+ 5% C_3H_8	6.7	2.4	26.5	62.9	93.2	–	100	2.7	–	30.1	–	41.0	–
+ 10% C_3H_8	12.3	8.5	28.2	53.9	62.9	91.2	99.6	8.1	5.9	26.9	53.1	54.5	75.8
T = 823 K, feed space velocity 1800 h^{-1}													
100% CH_4	5.1	5.6	36.6	54.2	92.4	97.0	–	5.4	6.3	35.4	50.1	81.2	80.7
+ 5% C_3H_8	0.6	1.8	35.0	63.2	99.1	98.5	99.9	1.9	0.6	35.7	53.1	64.1	76.6
+ 10% C_3H_8	0.3	1.5	32.3	66.2	99.2	99.6	99.9	1.4	1.7	31.0	50.2	58.2	70.3

23%, respectively, indicating that the catalyst is resistant to deactivation by carbon deposits. The recovery of H_2 through the membrane varied within 65–67%; that is, the membrane permeability to hydrogen was constant. According to chromatographic analysis, the permeate contained H_2 only, indicating the absence of defects in the membrane. Regarding the service life of the membrane, it retained the hydrogen permeability and was defect-free during all the experiments, the results of which are presented in this paper, lasting for about 350 h.

CONCLUSIONS

The reaction of steam reforming of methane and its mixtures containing 5 and 10% C_3H_8 on the industrial nickel catalyst NIAP-03-01 was investigated at steam/feedstock ratios 3 and 5 and space velocities of 1800 and 3600 h^{-1}. The results of the experiments with 100% CH_4 showed that by carrying out the reaction in a membrane reactor, high feedstock conversion can be achieved under mild conditions. At atmospheric pressure, $T = 823$ K, a space velocity of 1800 h^{-1}, and steam/methane ratios of 3–5, the methane conversion is 80–90%. With an increase in the rate of H_2 removal from the reaction mixture by evacuating the permeate, almost complete conversion of CH_4 is observed, the selectivity for CO_2 is more than 50%, and about 80% of H_2 is removed from the reaction medium. This result shows that in the membrane reactor, it is possible to convert mixtures of methane with the closest homologues, as demonstrated by the example of model mixtures containing 5 and 10% C_3H_8. The steam reforming of the mixtures was studied at atmospheric pressure, temperatures of 773 and 823 K, space velocities of 1800 and 3600 h^{-1}, and steam/feedstock ratios of 3 and 5. Under these conditions, the complete conversion of propane was observed. Simultaneously with the steam reforming of C_3H_8, methanation reactions can occur. Their occurrence is undesirable because it leads to a decrease in the conversion parameter. It has been established that under the chosen conditions, the formation of CH_4 occurs at a higher feed space velocity, which is 3600 h^{-1}. When the steam/feedstock ratio is 3, the formation of CH_4 is observed at 823 K. It is assumed that under these conditions, CH_4 is formed as a result of the irreversible hydrocracking reaction of C_3H_8. With an increase in this ratio to 5, methane is produced both at 773 and 823 K, as a result of the reversible CO_2 hydrogenation reaction. With an increase in the rate of H_2 removal by evacuating the permeate, the contribution of this reaction decreases, which leads to an increase in conversion. In general, the presented results show that it is possible to perform steam reforming of CH_4 mixtures containing up to 10% C_3H_8 in a membrane reactor. The study of steam reforming of a mixture of methane containing 5% C_3H_8 for 50 h at 823 K, a steam/feedstock ratio of 3, and a feed space velocity of 3600 h^{-1} has show that the catalytic system is not deactivated and the membrane retains H_2 permeability and remains defect-free. The results show that the most favorable conditions for the steam reforming of methane mixtures containing up to 10% C_3H_8 are the temperature of 823 K, the steam/feedstock ratio of 5, and the space velocity of 1800 h^{-1}. Under these conditions, when the permeate is subjected to vacuum pumping, the complete conversion of the feedstock is observed, the selectivity for CO_2 is 50%, and about 70% of H_2 is removed from the reaction mixture.

ACKNOWLEDGMENTS

This work was carried out under the 2013–2020 Program of Basic Research of State Academies of Sciences, theme code 0089-2014-0032.

REFERENCES

1. S. J. Peighambardoust, S. Rowshanzamir, and M. Amjjadi, J. Hydrogen Energy **35**, 9349 (2010).
2. S. A. Skrylev, Energ. Strateg., No. 2, 15 (2012).
3. I. V. Kozodoev, N. A. Kuzin, Yu. I. Amosov, et al., Ind. Ecol. North. **11**, 40 (2011).
4. G. S. Fal'kovich, N. N. Rostanin, L. M. Vilenskii, et al., Katal. Prom-sti, No. **3**, 10 (2003).
5. V. S. Arutyunov and O. V. Krylov, *Oxidative Conversion of Methane* (Nauka, Moscow, 1998) [in Russian].
6. K. Aasberg-Petersen, I. Dybkjaer, C. V. Ovesen, et al., J. Nat. Gas Sci. Eng. **3**, 423 (2011).
7. S. Yoon and J. Bae, Catal. Today **156**, 49 (2010).
8. X. Wang, X. Zou, X. Wang, et al., Int. J. Hydrogen Energy **36**, 4908 (2011).
9. B. T. Schadel, M. Duisberg, and O. Deutschmann, Catal. Today **142**, 42 (2009).
10. Y. Chen, Y. Wang, H. Xu, and G. Xiong, Appl. Catal., B **80**, 283 (2008).
11. M. Saric, Y. C. Delft, R. Sumbharaju, et al., Catal. Today **193**, 74 (2012).
12. J. Y. Matsumura and J. Tong, Top. Catal. **51**, 283 (2008).
13. G. Burkhanov, N. Gorina, N. Kolchugina, and N. Roshan, Platinum Met. Rev. **55**, 3 (2011).
14. L. Didenko, V. Savchenko, L. Sementsova, and L. Bikov, Int. J. Hydrogen Energy **41**, 307 (2016).
15. V. M. Ievlev, K. A. Solntsev, A. I. Dontsov, et al., Tech. Phys. **61**, 467 (2016).
16. V. M. Ievlev, A. A. Maksimenko, A. I. Sitnikov, et al., Materialovedenie, No. **2**, 37 (2016).
17. V. M. Ievlev, G. S. Burkhanov, A. A. Maksimenko, et al., Kondens. Sredy Mezhfaz. Granitsy **15**, 121 (2013).
18. Y. Shirasaki, T. Tsuneki, Y. Ota, et al., Int. J. Hydrogen Energy **34**, 4482 (2009).
19. L. P. Didenko, L. A. Sementsova, P. E. Chizhov, et al., Russ. Chem. Bull. **65**, 1997 (2016).

20. S. Campanari, E. Macchi, and G. Manzolini, Int. J. Hydrogen Energy **33**, 1361 (2008).
21. P. Ciavarella, D. Casanave, H. Moueddeb, et al., Catal. Today **67**, 177 (2001).
22. L. van Dyk, S. Miachon, L. Lorenzen, et al., Catal. Today **82**, 167 (2003).
23. S. Miachon and J.-A. Dalmon, Top. Catal. **29**, 59 (2004).
24. L. P. Didenko, V. I. Savchenko, L. A. Sementsova, and P. E. Chizhov, Pet. Chem. **56**, 459 (2016).
25. M. V. Zyryanova, P. V. Snytnikov, A. B. Shigarov, et al., Fuel **135**, 76 (2014).
26. M. M. Zyryanova, S. D. Badmaev, V. D. Belyaev, Yu. I. Amosov, P. V. Snytnikov, V. A. Kirillov, V. A. Sobyanin, Catal. Ind. **5**, 312 (2013).
27. B. T. Schadel, M. Duisberg, and O. Deutschmann, Catal. Today **142**, 42 (2009).
28. M. A. Rarib, J. R. Grace, C. J. Lim, and S. S. E. H. Elnashaie, Int. J. Hydrogen Energy **35**, 6276 (2010).

Translated by S. Zatonsky