Dehydrogenation of Propane in a Combined Membrane Reactor with Hydrogen-Permeable Palladium Module

L. P. Didenko, V. I. Savchenko, L. A. Sementsova, P. E. Chizhov, and L. A. Bykov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia

e-mail: ludi@icp.ac.ru Received July 3, 2012

Abstract—The basic features of the propane dehydrogenation reaction in a combined membrane reactor with a hydrogen-permeable palladium module and chromia–alumina catalyst (9.0 wt % Cr) in the temperature range of $520-580^{\circ}$ C have been studied. Under optimum conditions (*T*, 550° C; propane space velocity and a stripping gas flow rate of $600-900 \text{ h}^{-1}$ and $100-250 \text{ cm}^3/\text{min}$, respectively), the feedstock conversion to propylene increases by a factor of 1.6-2.0. It has been suggested that compliance between the rate of H₂ formation and its withdrawal through the membrane is of considerable importance.

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An alternative to the relevant petrochemical process for manufacturing olefins is catalytic dehydrogenation of light alkanes using natural gas, associated gas, and refinery gas as inexpensive and available feedstock, whose reserves are in great abundance, but the use is extremely inefficient. Because of endothermicity and thermodynamic limitations of the reaction, high temperatures are required for achieving acceptable vields. However, there are side reactions of feedstock cracking and hydrocarbon deposit formation occurring under these conditions, which reduce the selectivity for the desired products and lead to catalyst deactivation. For these reasons, the currently practiced processes for the manufacturing of olefins from light hydrocarbons are energy- and capital-intensive and require new engineering solutions to improve their performance.

One of these solutions is membrane technology. As a result of combining the reaction process and hydrogen removal from the reaction zone in a one membrane reactor, it is possible to increase the proportion of the desired product in the equilibrium product composition. Regarding the membrane material, palladium is of great interest since it possesses the highest H_2 selectivity. Note that monolithic palladium membranes (foil) have 100% hydrogen selectivity. However, their low mechanical strength is a disadvantage. To ensure the strength, a Pd foil thickness must be at least 50 µm, but the permeability of the foil is significantly reduced with such a thickness.

In this study, a Pd/Ag foil with a thickness of 30 μ m was used as a hydrogen permeable material. To prevent its destruction during operation, a disk from the foil was fixed between two metal grids with a thickness of

130 μ m made of finely weaved stainless steel with a mesh size of 2 μ m (Fig. 1).

Investigation of the technical characteristics of the resulting membrane module (MM) in the temperature range of $25-550^{\circ}$ C and a transmembrane pressure of up to 176.5 kPa showed that it has good thermal stability and mechanical strength parameter and is close to composite palladium membranes in properties (permeability, H₂ adsorption limitations to the performance, activation energy of permeability) it [1]. At the same time, its advantage is 100% hydrogen selectivity.

In this work, a palladium MM was used to remove H_2 from the products of the reaction of catalytic dehydrogenation of propane. The purpose of the work was to study the main features of this reaction by varying the temperature and the feedstock and stripping-gas flow rates.

EXPERIMENTAL

The reaction was carried out in a combined membrane reactor (Fig. 2) comprising a hydrogen-permeable module based on Pd/Ag foil (15.0 wt % Ag) of 30 μ m thickness produced by the technology designed at the Moscow special alloy processing plant The hydrogen-permeable module was placed between a feed-retentate supply chamber (*3*) and H₂ permeate withdrawal chamber (*I*). In compartment *3*, 1 cm³ (0.61 g) of a chromia–alumina catalyst (9.0 wt % Cr, grain fraction 0.2–0.4 mm) prepared by a modified coprecipitation technique was placed.

The catalyst used in the study was from one batch, and it was not subjected to regeneration.



Fig. 1. General view of the membrane module.

Propane (100%) was fed to the catalyst through inlets located on the periphery of reactor compartment 3, and the products were withdrawn through the central aperture and sent to a chromatograph. As a driving force for H_2 withdrawal through the membrane, a stripping gas, nitrogen, entered counter-currently to propane into compartment 1 of the reactor.

The gas streams were controlled by RRG-12 gas flow meters (Elektropribor, Zelenograd). The reactor was heated an electric oven. The temperature at the membrane and in the oven was monitored with chromel-alumel thermocouples. The product composition was analyzed in the on-line mode using a Kristall-5000 chromatograph with FID and thermal conductivity detectors. The H₂ content in the products was determined on a column with 13X molecular sieves (2 mm \times 2 m, 50°C, argon carrier gas). The hydrocarbon composition of the products was determined using a HP-Al/KCl column (0.5 mm \times 30 m, 80°C, helium carrier gas). The concentration of the products was calculated using the method of absolute calibration. The accuracy of the analysis was 99.2%. The propane conversion $(\alpha, \%)$ and the selectivity for products (S, %) were calculated by the formulae:

$$\alpha = \frac{X_{C_{3}H_{8}}^{in}V_{in} - X_{C_{3}H_{8}}^{out}V_{out}}{X_{C_{3}H_{8}}^{in}V_{in}} \times 100;$$

$$S = \frac{nX_{npoq}V_{out}}{3(X_{C_{3}H_{8}}^{in}V_{in} - X_{C_{3}H_{8}}^{out}V_{out})} \times 100,$$

where V_{in} is the propane volumetric flow rate at the reactor inlet, cm³/min; $X_{C_3H_8}^{in}$ is the volume concentration of propane in the gas stream at the reactor inlet, %; $X_{C_3H_8}^{out}$ is the volume concentration of propane in the products at the reactor outlet, %; V_{out} is the volumetric

flow rate of the products at the reactor outlet, cm^3/min ; X_{prod} is the volume concentration of a product in the mixture leaving the reactor, %; and *n* is the number of carbon atoms in the product.

The selectivity of the formation of hydrocarbon deposit (S_C , %) was calculated as:

$$S_{\rm C} = 100 - (S_{\rm CH_4} + S_{\rm C_2H_6} + S_{\rm C_3H_6})$$

where S_{CH_4} , $S_{C_2H_6}$, $S_{C_3H_6}$ are the selectivities for methane, ethane, and propylene, respectively, %.

The main characteristics of the reaction were studied at T = 520, 550 and 580° C and at various flow rates of feedstock and stripping gas. The effect of H₂ removal through the membrane on the propane conversion and the product composition was revealed in comparative experiments under the same conditions without H₂ removal, a gas-tight stainless steel plug was installed instead of the MM for this purpose.

RESULTS AND DISCUSSIONS

The principal propane dehydrogenation reaction :

$$C_3H_8 \longleftrightarrow C_3H_6 + H_2, \tag{1}$$

occurs in the test system, as well as side reactions of propane cracking and the formation of hydrocarbon deposit (HD).

Since both Pd/Ag foil and stainless steel grids can exhibit catalytic activity in the dehydrogenation of propane, experiments in the absence of the catalyst were run prior to the study. Measurements were made in the reactor with the membrane module at T =550°C and closed exit from the permeate compartment. It was found that in this case at a propane space velocity of 600 h⁻¹, the conversion was 0.9% and the selectivity for CH₄, C₂H₄, C₂H₆, C₃H₆, or HD was 11.5, 6.1, 3.1, 34.6, or 44.7%, respectively. Thus, the

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Fig. 2. Construction arrangement of the membrane reactor: (1) permeate compartment, (2) membrane module, (3) retentate compartment, and (4) supply and exhaust pipes.

dehydrogenation of propane on the foil and grid occurs to a small extent and almost does not affect the performance of the main reaction. Under the above specified conditions, the yield of propylene was about 30%.

Catalytic studies at $T = 520^{\circ}$ C, feeds flow rates of $5-15 \text{ cm}^3/\text{min}$ (from 300 h⁻¹ to 900 h⁻¹), and various flow rates of the stripping gas showed that the propane conversion is lower than in the "nonmembrane" reaction in all cases (Fig. 3). In this case, the CH₄ content in the product composition increases. The table shows the change in the CH₄/C₂H₆ ratio in the products at feed space velocity of 300 h⁻¹. One can see that this ratio increases upon the withdrawal of H₂ through the membrane, as well as with an increase in the stripping-gas flow rate.

Methane and ethane are formed by the propane cracking reaction:

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6. \tag{2}$$

An increase in the CH_4/C_2H_6 ratio indicates that there is an additional methane formation route. This route can be the interaction of intermediate, HD precursor forms with H₂ present in the system. It is known [3, 4] that because of the occurrence of this reaction, the yield of HD deactivating the catalyst decreases to a certain extent. The experimental data presented in the table indicate an increase in the feedstock conversion to HD in the membrane reactions, especially at the initial stage. But the contribution of the hydrogenolysis reaction is apparently insufficient for reducing the catalyst deactivation rate.

Data for the reaction run at a temperature of 550° C and a propane flow rate of $10 \text{ cm}^3/\text{min}$ (600 h^{-1}) are presented by curves *1*, *2*, *3* in Figs. 4a and 4b). One can see that in the experiments without hydrogen with-drawal (curves *I*), the yield of propylene in the begin-



Fig. 3. Time variation of propane conversion and H_2 content in the reaction mixture at $T = 520^{\circ}C$: (1) without H_2 stripping and (2) with H_2 stripping. C_3H_8 space velocity = 300 h⁻¹ (5 cm³/min). Stripping gas flow rates: (2) 60 and (3) 250 cm³/min.

ning of the reaction is $\sim 30\%$ and decreases with an increase in the reaction time to 24% as a result of gradual deactivation of the catalyst.

The removal of hydrogen through the membrane at a stripping-gas flow rate of 100 cm³/min results in an increase in the yield of propylene by a factor of 1.6. In

Time variation of the CH_4/C_2H_6 ratio in the products. $T = 520^{\circ}C$, feed flow rate, 5 cm³/min (300 h⁻¹)

Reaction time, min	CH ₄ /C ₂ H ₆		
	without H ₂ withdrawal	with H ₂ withdrawal	
		stripping gas flow rate, cm ³ /min	
		60	250
10	4.0	9.8	14.5
40	2.0	2.9	5.6
80	2.0	2.7	2.3
120	2.1	2.6	2.4

this case, the H_2 content in the products is reduced to 15% (curves 2), which corresponds to removal through the membrane of ca. 30% of the H_2 produced. The propylene yield decreases with time and becomes nearly equal to "nonmembrane" value by the 120th min. The C_3H_6 selectivity at the beginning of the reaction is 81%, the remainder being CH_4 , C_2H_6 and HD. A decrease in the yield of propylene can be due to deactivation of the catalyst by HD formed. The increase in their output when removing H_2 through the membrane is typical to almost all membrane-catalytic reactions. One of the main reasons for this is the decrease in the content of H_2 in the reaction mixture. In addition, in the test membrane–catalyst system

a decrease in the MM permeability can occur due to the formation of HD on the MM. To verify this assumption, the MM permeability was studied before and after the membrane-catalytic reaction. It was found that the permeability of the MM after the reaction decreases by 20–50% depending on the reaction conditions. After annealing of the grids in air at T =600°C, the original membrane permeability is restored. Thus, the decrease in the MM permeability is caused by the buildup of HD on the grids, whereas the Pd/Ag foil is resistant toward the deposition. Published data also show that the formation of HD does not occur on the surface of bulk Pd and Pd–Ag membranes [3].

The study of the effect of the stripping-gas flow rate on the membrane-catalytic reaction showed that its performance remains almost unchanged with an increase in the flow rate to 130 cm³/min, but the yield of C_3H_6 is nearly identical to the "nonmembrane" value at a flow rate of 40 cm³/min (Fig. 4, curve 3). Such an effect of the stripping-gas flow rate can be explained in terms of the results of the earlier study on the hydrogen permeability of the MM [1]. It was found that the H_2 permeability increases with an increase in the stripping gas flow rate to a certain limit, and the permeability curve reaches a limit at flow rates above 80 cm³/min and ceases to depend on the flow rate of the stripping gas, which can be explained by the maximum possible removal of hydrogen entering the permeate compartment, other conditions being fixed. Taking into account these data, it can be assumed that the rate of H_2 removal from the reaction mixture does not change as the stripping gas flow rate increases from 100 to 130 cm^3/min ; so, the change in the flow rate of the stripping gas in this interval does not affect the reaction performance. But the rate of H₂ removal from the reaction mixture decreases when the flow rate of the stripping gas decreases to $40 \text{ cm}^3/\text{min}$. As is seen from Figs. 4a and 4b (curves 3), it is accompanied by an increase in the H₂ content of in the reaction mixture, and the yield of C_3H_6 in this case is almost the same as that obtained in the experiments without removal of H_2 . That is, as the rate of H_2 removal through the MM decreases, there is no increase in the conversion of feedstock to propylene relative to the equilibrium rate.

To explain this experimental result one can refer to the published data [5-7]. They showed that the membrane-catalyst system is an integral unit, where a consistency between the rate of H₂ formation and its removal through the membrane is required. If it is absent, then the H_2 withdrawal rate (if the catalyst is not effective) or the rate of hydrogen transport across the membrane (if the permeability of the membrane is insufficient) is the limiting step of the membrane catalytic process. In either case, the excess conversion of the feedstock into the desired product with respect to the equilibrium values cannot be reached. Taking these data into account, we can assume that with a decrease in the stripping-gas flow rate to 40 cm³/min and, hence, in the rate of H₂ removal through the membrane, this consistency is violated. For this reason, the removal of H₂ does not increase the conversion of the feedstock to the target product.

As illustrated by curve 2 in Fig. 4a, the "membrane effect" caused by H₂ withdrawal through the membrane is reduced over time because of an increased HD yield. A longer "membrane effect" can be achieved by increasing the feedstock space velocity and, thus, reducing the time of its contact with the catalyst. This is demonstrated by the experiments at 550°C and a propane flow rate of 15 cm³/min (900 h⁻¹) (Fig. 5), which show that the deactivating effect of HD decreases. In the experiments without the removal of hydrogen, the yield of C_3H_6 is 13% at the beginning of the reaction and varies slightly with time (curve 2). The removal of hydrogen through the membrane increases the yield of C₃H₆ in the beginning of the reaction by more than twofold (curve 1). Moreover, the "membrane effect" persists for a long time and exceeds the equilibrium value by a factor of 1.5 at a time of 120 min.

At a propane flow rate of $5 \text{ cm}^3/\text{min} (300 \text{ h}^{-1})$ and, hence, an increased contact time of the feedstock with the catalyst, the yield of HD increases, which leads to rapid deactivation of both the catalyst and the MM. When H₂ is withdrawn through the membrane, the deactivating effect of HD further increases. The result is a decrease in the yield of propylene relative to the equilibrium value upon H₂ removal.

An increase in temperature has a similar effect. At $T = 580^{\circ}$ C, rapid deactivation of the membrane-catalyst system occurs in the beginning of the reaction, and the variation in feedstock and stripping-gas flow rates over a wide range does not increase the yield of C₃H₆ relative to the equilibrium value.

In general, the results of the study show that the optimization of reaction conditions is very important for the enhancement of feedstock conversion into the desired product. First of all, it is necessary to optimize the temperature for a maximum yield of the desired product to be achieved with minimal formation of hydrocarbon deposit. A difference in the activation energies of the principal reaction and the HD formation reaction makes it possible to reduce the buildup of



Fig. 4. Effect of H₂ removal through the membrane on propane conversion. $T = 550^{\circ}$ C, C₃H₈ flow rate 600 h⁻¹ (10 cm³/min). (*I*) without H₂ stripping and (*2*, *3*) with H₂ stripping. Stripping-gas flow rates: (*2*) 100 and (*3*) 40 cm³/min.

HD, maintaining a sufficiently high yield of olefins at an optimum temperature.

Catalyst deactivation by the HD is a serious problem in the dehydrogenation of alkanes, and upon the removal of H_2 through membrane this problem becomes more heavy due to increasing formation of HD. In this regard, the membrane–catalytic process requires frequent catalyst regeneration, and the retention of the catalytic activity after the regeneration is important. It has been shown [8] that the activity of chromia–alumina catalyst used in this work insignificantly changes after thermal treatment in air at 550°C and subsequent reduction with hydrogen at the same temperature.

The results of the present study also indicate an important role of optimization of the reaction with respect to the flow rate of the stripping gas. At fixed values of temperature and feed flow rate, the stripping-gas flow rate should provide the rate of H_2 transport across the membrane corresponding to the rate of its formation, which, by our assumption, is a necessary condition for increasing the yield of the desired prod-



Fig. 5. Time variation of propylene yield at a feed space velocity of 900 h⁻¹ and T = 550 °C: (1) without H₂ stripping and (2) with H₂ stripping at a stripping gas flow rate of 250 cm³/min.

uct relative to the equilibrium value. The optimum conditions in this system are $T = 550^{\circ}$ C, the feed space velocity of 600–900 h⁻¹, and the stripping gas flow rate of 100 cm³or higher. Under these conditions, the increase in the feedstock to propylene conversion makes 1.6–2 times the equilibrium value. In other cases, either a decrease in the H₂ formation rate because of catalyst deactivation by hydrocarbon deposit or reduction in the rate of H₂ removal through the membrane due to a decrease in the stripping gas flow rate are observed. In both cases, the correspondence between the catalyst and the membrane is broken and the "membrane effect" is not observed.

It is also of interest to compare the results with the published data on the membrane-catalytic dehydrogenation of propane using palladium membranes. As in this paper, the results of other studies indicate an important role of optimization of the feedstock and stripping-gas flow rates [9]. An increase in the yield of propylene relative to equilibrium values was obtained only at low feed rates, which is due to a low membrane permeability. Thus, in the case of using commercial tubular membrane made of Pd/Ag (25% Ag), the "membrane effect" was obtained only at propane space velocities of $0.1-0.15 \text{ h}^{-1}$ [3], which is ten times below that of feedstock in the commercial dehydrogenation process. Similarly, for the membrane-catalyst systems with composite membranes, an increase in the yield of propylene was obtained at low feed space velocities. For example, the yield of propylene at 500°C and a feed space velocity of 0.1 h^{-1} in [9] was 60-80%, much higher than the equilibrium value. However, the yield of C_3H_6 decreases with an increase in the propane space velocity and becomes comparable with the equilibrium value at a velocity of 0.8 h^{-1} or higher. The cited authors attribute this to the fact that at a propane space velocity of 0.8 h^{-1} or higher, the rate of withdrawal of H_2 becomes lower than the rate of its formation.

A major problem with composite palladium membranes is their rapid deactivation by coke at temperatures above 500°C. It was found that during coking, carbon is incorporated in the palladium membrane layer, thereby increasing the number of defects and, as a result, reducing both the membrane permeability and H₂ selectivity [10].

In general, analysis of the available results shows that further development of monolithic palladium membranes is promising. Their properties, such as high thermal stability, 100% hydrogen selectivity, and resistance to deactivation by hydrocarbon deposit, are important in the processes of high-temperature dehydrogenation of light hydrocarbon feedstock complicated by deposition of hydrocarbons.

Thus, the important role of optimization of conditions for the membrane–catalytic reaction of propane dehydrogenation on the temperature and the feed and stripping-gas flow rates in order to obtain the maximum yield of the desired product with minimal formation of hydrocarbon deposit was shown. It is suggested that in order to increase the feedstock conversion to the desired product, the rate of H₂ removal through the membrane should match the rate of its formation under the reaction conditions. Under optimal conditions ($T = 550^{\circ}$ C, a propane space velocity of 600– 900 h⁻¹, a stripping gas flow rate of >100 cm³/min), the yield of propylene in the membrane–catalytic reaction of propane dehydrogenation increases to 1.6–2.0 times the equilibrium value.

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