Dehydrogenation of *n*-Butane on the Industrial Microspherical Chromia–Alumina Catalyst AOK-73-24 in a Membrane Reactor

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Abstract—The basic features of the catalytic membrane dehydrogenation of *n*-butane have been studied in a reactor with membrane modules based on Pd/Ag foil of 9.3 and 30 μ m thickness and in the absence of the membrane (temperature, 500–550°C; feed space velocity, 150–1200 h⁻¹). It has been shown that in the absence of the membrane, the dehydrogenation of *n*-butane occurs in the kinetic region. The membrane thickness has a significant effect on the performance of the catalytic membrane reaction, presumably, because of the difference in the rate of H₂ withdrawal from the reaction mixture. In the reactor with the 9.3- μ m thick Pd/Ag-foil, the reaction proceeds to the diffusion region, thereby resulting in both enhancement of selectivity for butenes and a reduction of the yield of hydrocarbon deposits.

Keywords: palladium membrane module, catalytic dehydrogenation, *n*-butane, chromia–alumina catalyst **DOI:** 10.1134/S0965544113060054

Catalytic dehydrogenation of lower alkanes is an alternative petrochemical process for manufacturing the valuable chemicals olefins from inexpensive and available natural gas and petroleum gas feedstock, whose reserves are large and their use is highly ineffective.

The development of industrial processes for catalytic dehydrogenation of light hydrocarbon feedstock is hindered by their high energy and capital intensity due to the endothermicity of the reaction and thermodynamic constraints on the product yield. Thus, there is a need for new technological solutions aimed at enhancing the reaction performance, the feedstock conversion, and the selectivity for the desired products.

One of the solutions is the membrane technology. As a result of combining the reaction process with hydrogen removal from the reaction zone, the feedstock to olefin conversion may increase and the selectivity for cracking products can decrease. The concept of the catalytic membrane process was first formulated and implemented in studies by Academician V.M. Gryaznov and coworkers [1-6], which gave rise to a wealth of research in this field over the world.

The severe conditions of the dehydrogenation reaction impose high requirements on the membrane material, which should possess heat resistance, mechanical strength, and resistance to deactivation by hydrocarbon deposits, along with a high H_2 selectivity. From this standpoint, palladium is of the greatest interest since palladium foil has the 100% H_2 selectiv-

ity, thus opening the possibility of obtaining in principle the two desired products olefin and hydrogen in the catalytic membrane process of dehydrogenation of light alkanes.

Previously, we investigated the reaction of catalytic dehydrogenation of propane in a combination reactor with a membrane module based on Pd/Ag foil of a 30 μ m thickness and showed that as a result of H₂ removal from the reaction mixture, the yield of propylene increased by a factor of 1.6–2 [7]. In this study, the palladium membrane module was used for the removal of H₂ from the products of catalytic dehydrogenation of *n*-butane, another component of natural gas or petroleum gas.

The objective of this study was to reveal the basic features of the catalytic membrane dehydrogenation of n-butane on the industrial microspherical chromia-alumina catalyst AOK-73-24.

EXPERIMENTAL

The reaction was run in the combined membrane reactor including a hydrogen-permeable module based on Pd/Ag foil (15.0 wt % Ag); the foil was obtained by the process designed at the Moscow Specialty Alloy Processing Plant. The membrane modules MM 1 and MM 2 used had palladium foils of 9.3 and 30 μ m thickness, respectively. The designs of the reactor and the membrane module are detailed in [7, 8]. A 2 cm³ (2.3 g) portion of the industrial microspherical chromia–alumina catalyst AOK-73-24, prepared by

impregnating the hydrargillite thermochemical activation product with aqueous solutions of chromium and potassium salts (TU (Technical Specifications) 6-68-208-04), was placed in the retentate compartment of the reactor. In this study, we used the same batch of the catalyst and its regeneration was not practiced. *n*-Butane (100%) at a preset rate was fed on the catalyst through the holes located on the periphery of the retentate compartment, and the resulting products were withdrawn through the central hole and sent to a chromatograph. As a driving force for the removal of H₂ through the membrane, the stripping gas nitrogen was used, which was fed counter-currently to butane to the permeate compartment. The flow rates of the stripping gas, which corresponded to the maximum possible withdrawal of H₂ under the chosen conditions and were determined on the basis of a preliminary study of the hydrogen permeability of MM 1 and MM 2, were 40 and 150 cm³/min, respectively.

The gas flow rates were controlled with RRG-12 gas flow regulators (Electropribor, Zelenograd). The reactor was heated in an electric oven. The temperature on 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 flame-ionization and thermal conductivity detectors. The H₂ content in the products was determined on a column packed with molecular sieves 13X (2 mm \times 2 m; 50°C; carrier gas, argon). The hydrocarbon composition of the products was determined on an HP-Al/KCl column (0.5 mm \times 30 m; 80°C; carrier gas, helium). The amount of the products was calculated using the method of absolute calibration. The relative error of the analysis did not exceed 2%.

The conversion of butane $(\alpha, \%)$ and selectivity for products (S, %) were calculated by the following formulas:

$$\alpha = \frac{X_{C_4H_{10}}^{in} V_{in} - X_{C_4H_{10}}^{out} V_{out}}{X_{C_4H_{10}}^{in} V_{in}} \times 100,$$

$$S = \frac{nX_{\text{prod}} V_{out}}{4(X_{C_4H_{10}}^{in} V_{in} - X_{C_4H_{10}}^{out} V_{out})} \times 100,$$

where V_{in} is the volumetric flow rate of butane at the reactor inlet, cm³/min; $X_{C_4H_{10}}^{in}$ concentration of *n*-butane in the gas stream at the reactor inlet, volume %; $X_{C_4H_{10}}^{Bbix}$ is the concentration of *n*-butane at the reactor outlet, volume %; V_{out} is the volumetric flow rate of the products at the reactor outlet, cm³/min; X_{prod} is the concentration of the product in the mixture outflowing from the reactor, volume %; and *n* is the number of carbon atoms in the product molecule.

The yield of total butenes was calculated as the product of n-butane conversion and total butene

selectivity. The selectivity for the formation of hydrocarbon deposits ($S_{\rm C}$, %) was calculated as

$$S_{\rm C} = 100 - (S_{\rm CH_4} + S_{\rm C_2H_4} + S_{\rm C_2H_6} + S_{\rm C_3H_6} + S_{\Sigma C_4H_8}),$$

where $S_{C_2H_4}$, $S_{C_2H_6}$, $S_{C_3H_6}$, $S_{\Sigma C_2H_8}$ are the selectivities for methane, ethylene, ethane, propylene, and butenes, respectively, in %.

RESULTS AND DISCUSSION

The basic features of the reaction were studied by varying the temperature in the range of $500-550^{\circ}$ C and the feed space velocity within $150-1200 \text{ h}^{-1}$. The influence of H₂ removal through the membrane on the yield and composition of butenes was determined on the basis of the results of comparative experiments under the same conditions without H₂ withdrawal ("nonmembrane" reaction); for this purpose, a gastight stainless steel plug was installed instead of the membrane module.

The desired products of the catalytic dehydrogenation of *n*-butane were 1-butene, *trans*-2-butene, *cis*-2butene, and a small amount (2–4%) of 1,3-butadiene. The products also included H₂; the cracking products CH₄, C₂H₄, C₂H₆, and C₃H₆ gases; and hydrocarbon deposit (HCD).

Since both the Pd/Ag foil and stainless steel meshes can exhibit catalytic activity in the *n*-butane dehydrogenation reaction, blank runs in the absence of a catalyst were conducted prior to the study. The measurements were made in the membrane reactor at T =550°C with the closed exit from the permeate compartment. It was found that at a space velocity of 600 h⁻¹, the feedstock conversion was 1.2%. Thus, the dehydrogenation of *n*-butane on the foil and the mesh proceeds to a small extent, and barely affects the characteristics of the reaction

Figures 1a, 1b, and 1c present the results of the experiments without the withdrawal of H_2 from the reaction and with its withdrawal through MM 1 at a feed space velocity varied from 300 to 1200 h^{-1} . It can be seen that the yield of butenes in the nonmembrane reaction (Fig. 1a) does not depend on the feed space velocity, thereby suggesting the absence of diffusion control of the reaction under these conditions. At the same time, the yield of butenes in the catalytic membrane reaction increases with the feedstock space velocity to be $\sim 33\%$ at 900 h⁻¹ and remains actually unchanged with the further increase in the space velocity (Fig. 1b). The yield of HCD decreases from ~45% at a feed space velocity of 300 h^{-1} to ~18% at 900 h^{-1} or higher (Fig. 1c). Note that the HCD accumulates not only in the catalyst bed, but also partly on the surface of stainless steel mesh in the membrane module without affecting the Pd/Ag foil. To remove HCD after each run, the meshes were held in a muffle furnace at $T = 600^{\circ}$ C for four hours.

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Fig. 1. Effect of the feed space velocity on the yields of total C₄ butenes and hydrocarbon deposit at $T = 550^{\circ}$ C and a Pd/Ag foil thickness of 9.3 µm (a) without removal of H₂ and (b, c) with H₂ removed at a stripping gas flow rate of 40 cm³/min. *n*-Butane space velocity: (1) 300, (2) 600, (3) 900, and (4) 1200 h⁻¹.

In the membrane reactor with MM 2, the effect of the feedstock space velocity on the yield of butenes is substantially different. As can be seen from Fig. 2, the yield of butenes increases with a decrease in the space velocity and is ~ 54% at 150 h⁻¹ of butane. The specific feature of the reaction is a lower yield of HCD as compared with the nonmembrane process (Fig. 3). A reduction in the yield of HCD is not characteristic of the catalytic membrane reaction. Typically, the yield of HCD is higher in the case of H₂ withdrawal from the reaction mixture, a difference that is believed to be due to the weakening of the stabilizing effect of H₂ [9, 10].

The influence of temperature on the yields of butenes and HCD in the presence of the membrane module with the Pd/Ag-foil of varying thickness is illustrated in Table 1.

It can be seen that in the range of $500-550^{\circ}$ C, the yield of butenes increases by approximately a factor of 5 when MM 1 and MM 2 are used. The yield of HCD weakly depends on temperature in the reactor with MM 2, whereas it increases with the temperature in the case of MM 1. As a result, the selectivity for butenes is higher in the catalyst–MM 2 membrane system. From the data in Table 2 it is seen that the selectivity for 1-butene, *trans*-2-butene and *cis*-2-butene is higher in the reactor with MM 2, rather than MM 1; as the temperature increases, this difference increases.

The results of comparative runs of the catalytic membrane reaction with the MM 2 membrane and the nonmembrane reaction at various feedstock space velocities are presented in Figs. 4a and 4b. It can be

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seen that an increase in the yield of the desired products relative to the "nonmembrane" reference value is achieved only at low feedstock space velocity of 150 h^{-1} . The yield of butenes in the membrane process



Fig. 2. Effect of the feed space velocity on the yield of total C_4 butenes at $T = 550^{\circ}$ C. Foil thickness, 30 µm; stripping gas flow rate, 150 cm³/min. *n*-Butane space velocity: (1) 150 and (2) 900 h⁻¹.



Fig. 3. Yield of hydrocarbon deposit in experiments (1) with and (2) without H₂ withdrawal at a Pd/Ag foil thickness of 30 μ m, $T = 550^{\circ}$ C, and feed space velocities of (a) 150 and (b) 900 h⁻¹.

is \sim 55% under these conditions; however, it decreases with time and becomes equal to the "nonmembrane" value after 120 min.

In similar comparative experiments with the MM 1 membrane, the yield of butenes did not exceed the nonmembrane value at any feed space velocity. Figures 5a-5c show that the greatest difference between the catalytic membrane and nonmembrane reactions at 550° C is observed at a feed space velocity of 300 h^{-1} ; as the space velocity increases, the difference is reduce; at 500° C, it is negligible.

These results indicate a significant influence of the membrane module type (MM 1 or MM 2) on the yield of the desired products. Since these membranes differ in the Pd/Ag foil thickness and, hence, hydrogen permeability, it may be assumed that this is the main cause of the differences observed. Our earlier study [11] of the hydrogen permeability of MM 1 and MM 2 at $T = 400^{\circ}$ C showed that the permeability increases by a factor of 3.5 as the thickness of the Pd/Ag foil decreases

from 30 to 9.3 μ m. Consequently, the above-described differences in the characteristics of the reaction may be due to different rates of H₂ withdrawal through MM 1 and MM 2.

In the reactor with the MM 1 membrane having a higher H₂ permeability and, hence, a higher H₂ withdrawal rate, the yield of HCD is significantly greater, being ~45% at a butane space velocity of 300 h^{-1} and a temperature of 550°C; this leads to catalyst deactivation and, as a consequence, lowering the yield of butenes. An increase in the feed space velocity diminishes the deactivating effect of HCD by virtue of decreasing their amount; thus, the yield of butenes increases, approaching the nonmembrane value. The characteristics of the catalytic membrane and nonmembrane reactions at 500°C differ slightly. These data suggest that the process in the catalyst-MM 1 membrane system is controlled by the rate of formation of H_2 in the dehydrogenation reaction of *n*butane. Owing to the high H_2 permeability of the

Table 1. Influence of temperature on the yield of butenes and hydrocarbon deposit in the reactor with membrane modules with Pd/Ag foil of different thicknesses* at a feedstock space velocity of 1200 h^{-1} and stripping gas flow rates of 40 cm³/min (MM 1) and 150 cm³/min (MM 2)

Temperature, °C	500		550	
Foil thickness, μm	Butenes	HCD	Butenes	HCD
9.3	6.2	3.1	30.8	14.2
30	4.3	8.1	21.1	10.1
Without membrane	8.0	5.2	41.2	22.5

* Data by the 80th min of the reaction.

Temperature, °C	500		550	
Type of membrane module	MM 1	MM 2	MM 1	MM 2
Selectivity for butane-1, %	30.0	39.4	22.2	32.5
Selectivity for trans-butene-2, %	27.4	36.0	30.4	42.1
Selectivity for <i>cis</i> -butene-2, %	13.0	17.1	13.0	18.5

Table 2. Selectivity for the formation of butenes in the presence of membrane modules with Pd/Ag foil of different thicknesses^{*} at a feedstock space velocity of 1200 h⁻¹ and stripping gas flow rates of 40 cm³/min (MM 1) and 150 cm³/min (MM 2)

* Data by the 80th min of the reaction.

membrane, the H_2 removal rate can exceed the rate of its formation in the dehydrogenation reaction, and the latter is the rate-limiting step in the catalytic membrane process as a whole. For this reason, the "membrane effect", i.e., enhancement of the performance relative to the "nonmembrane" reaction, cannot be achieved. This result suggests an important role of the catalyst in the catalytic membrane system, as has been noted in a number of studies [12–14]. For a productive catalytic membrane system to be obtained, a high-permeability membrane should be combined with a highperformance catalyst.

On passing to the MM 2 membrane based on the Pd/Ag foil of a 30 μ m thickness, the rate of H₂ withdrawal from the reaction mixture decreases and the features of the catalytic membrane reaction in question are significantly altered. First of all, its occurrence region changes: in contrast to the nonmembrane reaction occurring in the kinetic region, the catalytic membrane reaction proceeds to the diffusion region, as indicated by the effect of the feed space velocity on the vield of butenes over the entire range examined. The increase in the yield of butenes with respect to the nonmembrane value at a feed space velocity of 150 h⁻¹ and 550°C cannot be called "membrane effect" in the strict sense of the word. The increase is associated with the different effects of the space velocity on the parameters of these reactions. Whereas the vield of butenes in the nonmembrane reaction is independent of the feed space velocity over the velocity range examined, that in the catalytic membrane process increases with the decreasing space velocity of butane, i.e., with an increase in the time of its contact with the catalyst, and becomes higher than the nonmembrane value at a space velocity of 150 h^{-1} .



Fig. 4. Change in the yield of total butenes in the comparative experiments (1) with H₂ withdrawal (stripping gas flow 150 cm³/min) and (2) without H₂ withdrawal at a Pd/Ag foil thickness of 30 µJm, $T = 550^{\circ}$ C, and feed space velocities of (a) 150 and (b) 900 h⁻¹.

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Fig. 5. Yield of total butenes in the (1) catalytic membrane and (2) "nonmembrane" reactions. Foil thickness, 9.3 μ m. *n*-Butane space velocity: (a) 300 or (b, c) 1200 h⁻¹.

Thus, it has been shown that the catalytic membrane dehydrogenation of *n*-butane on the industrial microspherical chromia-alumina catalyst AOK-73-24 significantly differs in features when Pd/Ag membranes of various thicknesses are used, with the differences being likely due to the different rates of H₂ withdrawal from the reaction mixture. It is assumed that the reaction with the use of the membrane module based on the Pd/Ag-foil of a 9.3 µm thickness is limited by the H₂ formation rate. The catalytic membrane reaction in the reactor with the Pd/Ag foil of a 30 µm thickness occurs in the diffusion region. With this foil, the yield of the hydrocarbon deposit is lower, a case that is untypical of the membrane dehydrogenation of alkanes; as a result, a higher selectivity for butenes is observed. The yield of total butenes of about 55%, which is greater than that in the nonmembrane process, has been achieved in the reactor with the membrane module based on palladium foil of a 30 µm thickness at $T = 550^{\circ}$ C and a feed space velocity of $150 h^{-1}$.

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REFERENCES

- 1. V. M. Gryaznov, Dokl. Akad. Nauk SSSR 189, 794 (1969).
- 2. V. M. Gryaznov, SU Patent No. 274,092 (1964).
- N. N. Mikhalenko, E. V. Khrapova, and V. M. Gryaznov, Zh. Fiz. Khim. 60, 511 (1986).
- 4. V. M. Gryaznov, M. M. Ermilova, L. S. Morozova, et al., J. Less-Comm. Met. **89**, 529 (1983).
- N. V. Orekhova, M. M. Ermilova, and V. M. Gryaznov, Dokl. Akad. Nauk SSSR 321 789 (1991).
- 6. E. M. Chistov, A. P. Mischenko, N. R. Roshan, and V. M. Gryaznov, in *Abstracts of the Second Conference on Catalysis in Membrane Reactors* (Moscow, 1996).
- 7. L. P. Didenko, V. I. Savchenko, L. A. Sementsova, et al., Pet. Chem. **53**, 27 (2013).
- 8. L. P. Didenko, M. S. Voronetskii, L. A. Sementsova, et al., Al'tern. Energ. Ekol., No. 10, 154 (2010).
- M. Sheintuch and R. M. Dessau, Chem. Eng. Sci. 51, 535 (1996).
- J. P. Collins, R. W. Schwartz, R. Sehgal, et al., Ind. Eng. Chem. Res. 35, 4398 (1996).
- 11. L. P. Didenko, V. I. Savchenko, V. V. Barelko, and L. A. Bykov, Al'tern. Energ. Ekol. (2013) (in press).
- P. Ciavarella, D. Casanave, S. Moueddeb, et al., Catal. Today 67, 177 (2001).
- 13. S. Miachon and J. A. Dalmon, Top. Catal. **29**, 59 (2004).
- D. Casanave, P. Ciavarella, and K. Fiaty, Chem. Eng. Sci. 54, 2807 (1999).

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