Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2021, **31**, 230–232

Mendeleev Communications

Increasing the yield of aromatic hydrocarbons in aromatization of *n*-butane over Ga/H-ZSM-5 zeolite using a palladium membrane

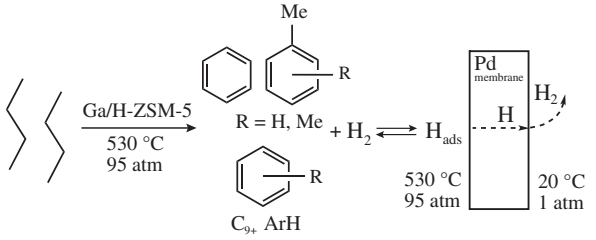
Viktor I. Bogdan,*[a,b] Aleksey E. Koklin,[a] Igor I. Mishanin,[a] Tatiana V. Bogdan,[a,b] Nikolay V. Mashchenko[a] and Leonid M. Kustov*[a,b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: vibogdan@gmail.com, lmk@ioc.ac.ru*

[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2021.03.028

The successful use of a palladium membrane to enhance the yield of benzene–toluene–xylene (BTX) fraction in *n*-butane aromatization at 530 °C and 95 atm on a Ga/H-ZSM-5 catalyst has been shown. Removal of hydrogen from the reaction zone through the palladium membrane led to an increase in both the *n*-butane conversion and the selectivity of the BTX fraction formation.



Keywords: aromatization, *n*-butane, palladium membrane, ZSM-5, Ga/H-ZSM-5, zeolite, BTX fraction, supercritical conditions.

The aromatization of light alkanes to obtain the benzene–toluene–xylene (BTX) fraction is a promising direction in the development of modern science and technology in the field of value-added hydrocarbon production.[1,2] The most effective for this process are bifunctional catalysts based on ZSM-5 zeolite containing a promoter metal, primarily gallium and zinc, alone or with the addition of a second transition metal.[3–5] The selectivity of aromatization of C_3/C_4 hydrocarbons on modified ZSM-5 zeolites is about 60–70%. This process has two significant disadvantages: first, a rapid deactivation of the catalyst due to the formation of coke and, secondly, the excessive formation of light C_1–C_4 hydrocarbons as a result of cracking or hydrogenolysis reactions.[6,7] The developed industrial processes of aromatization of light hydrocarbons, such as M2 forming (Mobil), Cyclar (UOP-BP), Aroforming (IFP-Saluted), are not widely used. The main disadvantage of these processes is significant coking on catalysts. Long-term stable operation requires continuous regeneration of catalysts to remove carbon deposits (coke) and by-products from the catalyst surface. In recent years, the production of BTX from alternative renewable raw materials (*e.g.*, ethanol,[8] glycerol[9] and ethyl acetate[10]) has been reported. However, catalyst deactivation remains an unsolved problem, and this raw material itself is much more valuable than light alkanes.

As previously reported,[11,12] carrying out aromatization under supercritical conditions (at 530 °C and 190 atm) can prevent the catalyst deactivation. Under the conditions of aromatization of supercritical butane, stable operation of catalysts based on ZSM-5 zeolite is observed.[12]

In this work, we investigated the effect of hydrogen removal from the reaction zone using a Pd membrane during the aromatization of *n*-butane on a Ga/H-ZSM-5[†] catalyst.

It should be noted that Ga/H-ZSM-5 catalyst used in this research is well known. Ga-modified high-silica zeolite H-ZSM-5 has been studied for decades and has also been utilized in the commercial aromatization process UOP Cyclar.[13,14] In particular, the Ga/H-ZSM-5 catalyst for the aromatization of light paraffins, especially effective for the conversion of propane and butane, was the subject of our publications in the 1990s.[15,16] According to diffuse-reflectance IR spectroscopy using adsorbed probe molecules (H_2, CH_4 *etc.*) and X-ray photoelectron spectroscopy, gallium in zeolite is present in two states, Ga^{3+} and Ga^{+}, which act as strong Lewis acid–base pair sites, responsible for the initial stage of the aromatization process, *i.e.*, the dehydrogenation of the substrate to produce primary olefinic species. Although a Pd membrane has already been used in many catalytic studies[17–19] to remove hydrogen from the reaction zone, we combined for the first time the butane aromatization process under supercritical conditions and the use of a Pd membrane for hydrogen removal to maximize the yield of aromatic hydrocarbons.

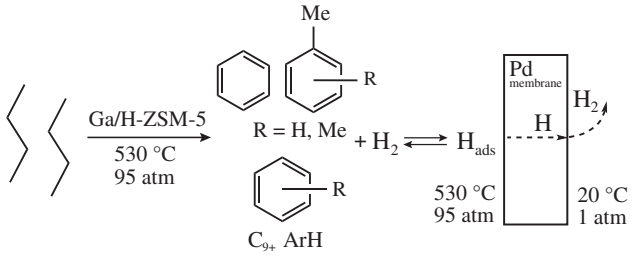
Aromatization of *n*-butane at high temperatures is a multistage process. The first stage is the formation of butenes from the original butane, a reaction that limits the rate of the entire process. The olefins rapidly oligomerize to larger intermediates, which are further cyclized to naphthenes. And the last stage is the dehydrogenation of naphthenes to aromatic hydrocarbons. A temperature of 500 °C or more is necessary because the aromatization involves the formation of butenes in the first stage, favored by a higher temperature. Theoretically, the aromatization of *n*-butane into xylenes occurs according to the total reaction equation:

$$2C_4H_{10} \rightleftharpoons Me\text{–}C_6H_4\text{–}Me + 5H_2, \quad (1)$$

[†] We used a commercial sample of zeolite ZSM-5 (Süd-Chemie, Si/Al = 25). The Ga/H-ZSM-5 catalyst contained 2 wt% of gallium. The H-form of zeolite was obtained by thermal decomposition of the NH_4-form. The H-form of zeolite was modified with gallium by impregnating in an aqueous solution of the calculated amount of gallium nitrate [$Ga(NO_3)_3$, Acros] at 80 °C for 4 h with stirring. Then the solvent was removed *in vacuo*, and the precipitate was dried at 120 °C and calcined in an air flow at 450 °C. Thereafter, the powder was pressed and crushed, and then a fraction of particles with a size of 0.25–0.50 mm was selected. Before the catalytic test, the catalyst was activated in a flow of hydrogen at 450 °C.

where 5 moles of hydrogen are formed per 2 moles of the original hydrocarbon. During aromatization, the reaction volume significantly increases due to the released hydrogen. Therefore, in order to shift the equilibrium towards aromatic products and, as a consequence, to increase the selectivity to BTX and other aromatic hydrocarbons, it is necessary to remove the hydrogen evolved as a result of the dehydrocyclization reaction. One of the methods for the selective extraction of hydrogen from the reaction zone is the use of palladium membranes. In principle, the palladium surface can act as a dehydrogenation catalyst, but then the reaction rate would be too slow due to the extremely small surface area. Thus, the Pd membrane is involved only in the removal of hydrogen from the reaction zone and does not perform the primary catalytic function.[19] Pure palladium undergoes embrittlement due to the hydride phase transition when exposed to hydrogen at temperatures below 300 °C.[20] The aromatization process and the accompanying hydrogen evolution occur at temperatures above 500 °C. Nevertheless, certain precautions must be taken due to the hydrogen embrittlement effect of Pd membranes. The experiment is shown in Scheme 1.

The catalytic tests of *n*-butane aromatization were performed at a temperature of 530 °C and a pressure of 1 or 95 atm.‡ The critical parameters of *n*-butane are 152 °C and 37 atm. Thus, at 530 °C and 95 atm, it can be considered as a supercritical fluid. The butane conversion and selectivities to main products on the Ga/H-ZSM-5 catalyst with and without a Pd membrane in the reaction zone are presented in Table 1 and Figure 1. The products



Scheme 1 Aromatization of *n*-butane using a Pd membrane.

Table 1 *n*-Butane aromatization on Ga/H-ZSM-5 in the presence and absence of a Pd membrane (530 °C, time on stream of 3 h).

Catalyst	*P*/ atm	GHSV (NTP)/ h^{-1}	Conversion (%)	Selectivity (%)			
				C_1–C_4	C_5–C_8	BTX	C_{9+} ArH
Ga/H-ZSM-5	1	400	91	38	0	53	9
Ga/H-ZSM-5	95	7300	65	66	6	17	11
Ga/H-ZSM-5 with Pd membrane	95	7300	87	59	3	23	15

‡ Catalytic experiments were performed at a temperature of 530 °C and atmospheric or elevated pressure (95 atm) in a flow-type fixed-bed stainless steel reactor with an inner diameter of 10 mm. The catalyst was mixed with quartz of the same grain in the ratio of 1 : 3. The free volume of the reactor was filled with quartz particles. The catalyst was heated to the required temperature in a flow of helium. Then *n*-butane was supplied using a gas flow regulator (at 1 atm) or a syringe liquid pump (at 95 atm). The pressure was regulated by a needle valve. The feed of *n*-butane in the experiments at 1 atm was 0.97 g h^{-1} cm^{-3} cat., which corresponds to the gas hourly space velocity (GHSV) of 400 h^{-1} (NTP), and at 95 atm –17.8 g h^{-1} cm^{-3} cat. or 7300 h^{-1} (NTP). A palladium capillary with an outer diameter of 1 mm and a wall thickness of 0.2 mm was used as a Pd membrane. It was sealed on one side, and its outlet was connected to a gasometer. The duration of the experiments was 4–5 h. The reaction products were analyzed by gas chromatography on a capillary column (100 m) with the OV-101 phase. The products were identified by gas chromatography–mass spectrometry.

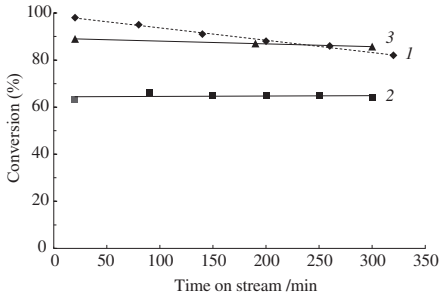


Figure 1 *n*-Butane conversion on Ga/H-ZSM-5 at 530 °C and a pressure of (*1*) 1 and (*2,3*) 95 atm (*1,2*) in the absence and (*3*) in the presence of a palladium membrane. GHSV was (*1*) 400 and (*2,3*) 7300 h^{-1}.

consisted of both aromatic hydrocarbons such as BTX fraction, ethylbenzene and others with 9 carbon atoms or more, including naphthalenes (C_{9+} ArH), and aliphatic hydrocarbons C_1–C_4 (methane, ethane, ethylene, propane, propylene, isobutane and butenes) and C_5–C_8 (alkanes and olefins).

Figure 1 demonstrates that the catalyst stability is improved under supercritical conditions (at 95 atm) compared to the gas phase. This is probably due to the continuous removal of coke precursors, which are washed out from the catalyst by supercritical *n*-butane.[11] While maintaining a high degree of butane conversion over time, the presence of a Pd capillary in the reaction zone increases the conversion from 65 to 87%. Also it increases the selectivity to BTX from 17 to 23% and the total selectivity to aromatic hydrocarbons by 10%. At the same time, the yield of aliphatic products, *viz.* cracking gas and C_{5+} hydrocarbons, decreases.

Figure 2 shows the time variations in hydrogen evolution under reaction conditions in the presence of a Pd membrane. Whithin 4 h of the experiment, up to 570 ml of hydrogen was evolved (Figure 2, curve *1*). The average rate of hydrogen evolution (Figure 2, curve *2*) during the aromatization of supercritical butane is about 5 times slower than the theoretically possible value.§ This is probably why the increase in the content of the BTX fraction in the reaction products was not so significant. In addition, the slight slope of curve *2* (see Figure 2), indicating a decrease in the rate of hydrogen evolution in a real experiment, can be associated with a small deposition of carbon on the surface of the Pd capillary. Palladium is subjected to deactivation by deposition of carbonaceous residues at

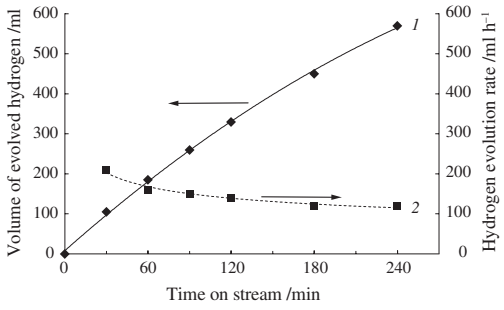


Figure 2 Time course of hydrogen evolution during *n*-butane aromatization on Ga/H-ZSM-5 in the presence of a Pd membrane (530 °C, 95 atm, GHSV = 7300 h^{-1}): (*1*) the total volume of evolved hydrogen and (*2*) the rate of hydrogen evolution.

§ A theoretically possible value for the hydrogen evolution rate was calculated as follows: V_{max} = *n*-butane feed [mol h^{-1}] × conversion × selectivity to BTX × 5/2 × volume of 1 mol gas at NTP. The 5/2 factor follows from the reaction equation for the conversion of butane to xylenes. The V_{max} value was 735 ml h^{-1}.

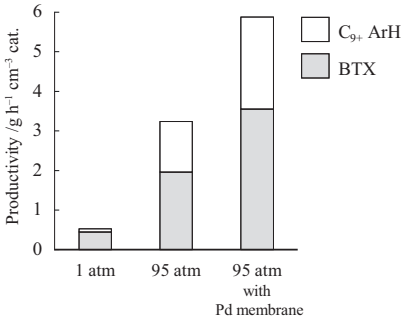


Figure 3 Productivity to the BTX and C_{9+} aromatic hydrocarbons during *n*-butane aromatization on Ga/H-ZSM-5 in the absence and presence of a Pd membrane at 530 °C and a pressure of 1 (GHSV = 400 h^{-1}) and 95 atm (GHSV = 7300 h^{-1}).

temperatures above 450 °C.[18,20] A decrease in the hydrogen permeability of the palladium membrane could occur due to the carbonization of its surface.

It is of note that moving from the gas-phase conditions (1 atm) during the high-temperature conversion of *n*-butane to supercritical conditions (95 atm) leads to a significant decrease in the selectivity to BTX and C_{9+} aromatic hydrocarbons and, at the same time, to a twofold increase in the selectivity to gas cracking products. If the catalytic aromatization of *n*-butane was carried out under supercritical conditions in the presence of a Pd membrane, then the selectivity to aromatic hydrocarbons becomes higher with a significant improvement in the performance of catalyst, in particular its productivity. According to Figure 3, the overall productivity to aromatic products under supercritical conditions increases by a factor of ~6, and under supercritical conditions with a Pd membrane, by a factor of ~11 as compared to the gas phase.

Thus, the data obtained demonstrate that the use of a Pd membrane to remove hydrogen evolved during the aromatization (dehydrocyclization) of *n*-butane in combination with supercritical conditions for *n*-butane can significantly increase, by an order of magnitude, the productivity of the aromatization process, as well as the stability of the catalyst compared to the gas-phase process.

References

1 K. M. Minachev and A. A. Dergachev, *Russ. Chem. Rev.*, 1990, **59**, 885 (*Usp. Khim.*, 1990, **59**, 1522).
2 Y. Ono, *Catal. Rev.: Sci. Eng.*, 1992, **34**, 179.
3 L. M. Lubango and M. S. Scurrell, *Appl. Catal., A*, 2002, **235**, 265.
4 G. G. Oseke, A. Y. Atta, B. Mukhtar, B. Y. Jibril and B. O. Aderemi, *Appl. Petrochem. Res.*, 2020, **10**, 55.
5 K. Frey, L. M. Lubango, M. S. Scurrell and L. Guczi, *React. Kinet., Mech. Catal.*, 2011, **104**, 303.
6 P. Mériaudeau and C. Naccache, *Catal. Rev.: Sci. Eng.*, 1997, **39**, 5.
7 G. Giannetto, R. Monque and R. Galiasso, *Catal. Rev.: Sci. Eng.*, 1994, **36**, 271.
8 Z. Li, A. W. Lepore, M. F. Salazar, G. S. Foo, B. H. Davison, Z. Wu and C. K. Narula, *Green Chem.*, 2017, **19**, 4344.
9 S. He, K. Zuur, D. S. Santosa, A. Heeres, C. Liu, E. Pidko and H. J. Heeres, *Appl. Catal., B*, 2021, **281**, 119467.
10 A. G. Dedov, A. A. Karavaev, A. S. Loktev, A. S. Mitinenko, I. E. Mukhin, E. A. Isaeva, E. V. Rogaleva and I. I. Moiseev, *Mendeleev Commun.*, 2020, **30**, 459.
11 E. S. Alekseev, A. Yu. Alentiev, A. S. Belova, V. I. Bogdan, T. V. Bogdan, A. V. Bystrova, E. R. Gafarova, E. N. Golubeva, E. A. Grebenik, O. I. Gromov, V. A. Davankov, S. G. Zlotin, M. G. Kiselev, A. E. Koklin, Y. N. Kononevich, A. E. Lazhko, V. V. Lunin, S. E. Lyubimov, O. N. Martyanov, I. I. Mishanin, A. M. Muzafarov, N. S. Nesterov, A. Y. Nikolaev, R. D. Oparin, O. O. Parenago, O. P. Parenago, Y. A. Pokusaeva, I. A. Ronova, A. B. Solovieva, M. N. Temnikov, P. S. Timashev, O. V. Turova, E. V. Filatova, A. A. Philippov, A. M. Chibiryaev and A. S. Shalygin, *Russ. Chem. Rev.*, 2020, **89**, 1337.
12 A. E. Koklin, A. N. Kalenchuk, N. V. Mashchenko, V. V. Lunin and V. I. Bogdan, *Russ. J. Phys. Chem. B*, 2020, **14**, 1277 [*Sverkhkriticheskie Flyuidy. Teoriya i Praktika*, 2020, **15** (2), 59].
13 M. Guisnet, N. S. Gnep and F. Alario, *Appl. Catal., A*, 1992, **89**, 1.
14 A. Bhan and W. N. Delgass, *Catal. Rev.: Sci. Eng.*, 2008, **50**, 19.
15 V. Kanazirev, R. Dimitrova, G. L. Price, A. Y. Khodakov, L. M. Kustov and V. B. Kazansky, *J. Mol. Catal.*, 1991, **70**, 111.
16 A. Y. Khodakov, L. M. Kustov, T. N. Bondarenko, A. A. Dergachev, V. B. Kazansky, K. M. Minachev, G. Borbély and H. K. Beyer, *Zeolites*, 1990, **10**, 603.
17 J. Shu, B. P. A. Grandjean, A. Van Neste and S. Kaliaguine, *Can. J. Chem. Eng.*, 1991, **69**, 1036.
18 M. R. Rahimpour, F. Samimi, A. Babapoor, T. Tohidian and S. Mohebi, *Chem. Eng. Process.*, 2017, **121**, 24.
19 R. Dittmeyer, V. Höllein and K. Daub, *J. Mol. Catal. A: Chem.*, 2001, **173**, 135.
20 S. K. Gade, P. M. Thoen and J. D. Way, *J. Membr. Sci.*, 2008, **316**, 112.

Received: 30th November 2020; Com. 20/6380