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n-Butane Isomerization in the Gas Phase and under Supercritical Conditions

V. I. Bogdan, E. G. Khelkovskaya-Sergeeva, T. V. Vasina, and V. B. Kazanskii
Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
E-mail: bogdan@ioc.ac.ru

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Abstract—The aromatization of *n*-butane under supercritical conditions on gallium-, zinc-, and platinum-modified high-silica zeolites with a modulus of 30–70 was first studied, and the experimental data were compared to the results of a study of this process in the gas phase. It was found that the operational efficiency of catalysts for *n*-butane conversion under supercritical conditions was much higher than that for the gas-phase reaction in terms of activity, productivity, and resistance to poisoning by condensation products. The aromatization of gaseous *n*-butane at 530°C and 1 atm was characterized by rapid catalyst deactivation. The selectivity for the benzene–toluene–xylene (BTX) fraction was higher than 50%. Under supercritical conditions at 430–560°C and 100–200 atm, the selectivity of formation of aromatic compounds decreased by a factor of 2, whereas the yield of C_1–C_3 cracking products increased by the above factor. On the other hand, it was found that an increase in the productivity of catalysts by a factor of 20–50 with the retention of almost 100% activity for several days of operation is an advantage of the process performed under supercritical conditions. The almost complete conversion of butane under supercritical conditions was found on promoted HZSM-5 zeolite samples. The thermogravimetric analysis of spent samples suggested a higher degree of catalyst carbonization under supercritical conditions, as compared with that in the reaction performed in the gas phase. However, the deposition of 20–30 wt % condensation products on the catalysts had no detectable effect on the high activity of the catalysts in the reaction performed under supercritical conditions.

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INTRODUCTION

The liquefaction of light alkanes by oligomerization and aromatization is a problem of considerable current interest. The results of studies of the gas-phase aromatization of light alkanes on hydrogen and modified forms of pentasils have been considered in detail in reviews [1, 2]. Leading chemical companies have their own processes for the aromatization of propane–butane raw materials. Thus, UOP developed the Cyclar process for the dehydrocyclodimerization of C_3–C_4 gases on high-silica zeolites modified with zinc and gallium at temperatures higher than 425°C with a yield of aromatic compounds up to 60–65% [3]. However, this technology has not found wide industrial use. This can be due to the following reasons: (1) low gaseous-alkane space velocities in the range 100–500 h^{-1} cannot provide reasonable productivity of the process and (2) rapid catalyst carbonization at reaction temperatures higher than 500°C results in rapid catalyst deactivation.

Previously, we found that the catalytic conversion of hydrocarbons under supercritical conditions is characterized by the almost complete absence of catalyst poisoning due to carbonization and by a much higher productivity of corresponding processes [4–7]. In this context, it would be hoped that a reaction performed under supercritical conditions could also be favorable in the case of the aromatization of light paraffins. Thus, the aim of this work was to perform the catalytic aromatization of *n*-butane under supercritical conditions and to compare the resulting characteristics with the corresponding reaction parameters in the gas phase.

EXPERIMENTAL

Zeolites and Zeolite-Based Catalysts

The H form of a pentasil ZSM-5 zeolite catalyst (Süd Chemie AG PPL6251E-5) with a modulus of 50 was used in this study. Zn, Ga, and Pt were used as modifying additives.

The zeolite catalysts were modified by the ion exchange of the hydrogen form of the zeolite in an aqueous solution of platinum ammonia complexes at 80°C for 4 h. Then, the solution was removed on a rotary evaporator and the precipitate was dried at 120°C, calcined in a flow of air at 450–500°C, and reduced with hydrogen at 450°C. The Zn- and Ga-containing zeolites were prepared analogously using aqueous solutions of zinc nitrate and gallium nitrate, respectively, for ion exchange.

Catalytic Tests, Reaction Product Analysis, and the Determination of Catalyst Coking

The catalytic properties of zeolites at atmospheric pressure were experimentally studied using a laboratory setup based on KL-1 and KL-2 catalytic units designed at the Special Design Bureau of the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences. Catalysts were loaded into a stainless-steel flow tube reactor 5 mm in diameter or a quartz reactor 4 mm in diameter. The temperature was controlled to within ±0.4 K, and the furnace was heated with a Miniterm 400.31 temperature regulator (OAO MZTA). The catalyst was heated to the required temperature in a flow of helium.

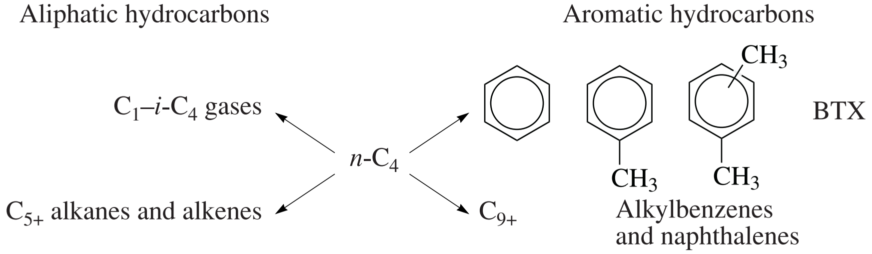
To perform catalytic experiments under supercritical conditions, the catalysts were loaded into stainless-steel flow reactors rated at a maximum pressure of 300 atm; the reactors were 3–10 mm in diameter depending on the weight of the catalyst sample. The pressure in the system was produced by supplying liquid butane with the use of an HPP 5001 liquid piston pump (Laboratorni pristroje, Prague, Czech Republic). Precise pressure adjustment at the reactor outlet was performed with high-pressure needle or membrane valves. The pressure in the system to 250 atm was measured with a reference pressure gage. The inlet and outlet lines in the KL-1 unit were thermostatically controlled at 200°C.

The simultaneous analysis of liquid and gaseous products was performed on an OV-101 capillary column 100 m in length. The separate analysis of gaseous products was performed with the use of columns 3–8 m in length packed with SKT active carbon, CaA molecular sieves, Al_2O_3, Porapak N, Porapak Q, Porapak P, PPMS, or Celite C-22. In particular cases, the reaction products were identified by chromatography–mass spectrometry.

The quantitative determination of the degree of coking of deactivated catalysts was performed by combined thermogravimetry and differential thermal analysis (TG–DTG–DTA) using an MOM derivatograph C under conditions of linear heating to 600–800°C at a rate of 10 K/min in air. Samples of 40–60 mg were placed in platinum crucibles. γ-Al_2O_3 was used as the reference.

RESULTS AND DISCUSSION

At temperatures higher than 400°C, *n*-butane undergoes the following catalytic transformations:



The oligomerization of alkanes followed by cracking with simultaneous isomerization results in the appearance of, on the one hand, cracked gas (methane, ethane, ethylene, propane, propylene, isobutane, and butylenes) in the reaction products and, on the other hand, normal and isomeric paraffins and olefins with five or more carbon atoms. The second direction of the high-temperature conversion of light alkanes is dehydrocyclization with the formation of aromatic hydrocarbons. These are primarily butane dehydrocyclodimerization products: benzene, toluene, isomeric xylenes, and ethylbenzene (BTX fraction). In addition, C_{9+} polyalkylbenzenes and highly condensed products (naphthalenes and alkylnaphthalenes) are formed. The direction of these processes depends on the nature of catalysts used and on reaction conditions. In the extensive literature on the aromatization of light alkanes, it has been noted that an increase in the reaction pressure of dehydrocyclization impairs the yields of aromatic products. This is most likely due to the fact that the increase of pressure in the system that increases in volume because of hydrogen formation shifts the reaction equilibrium to the left. In this case, the yield of aromatization products decreases, as compared with that in the reaction performed at atmospheric pressure.

Based on three-parameter correlations developed by Pitzer, we calculated isotherms for the pressure dependence of the reduced density of *n*-butane [8]. These isotherms indicate that, at a temperature higher than 450°C, the supercritical state of *n*-butane with a relative density of 0.5–1 corresponds to pressures higher than 140–150 atm. These pressures were chosen to study the high-temperature conversion of *n*-butane under supercritical conditions.

Figure 1 shows the time dependence of *n*-butane conversion on the gallium-modified HZSM-5 zeolite at various pressures.

As follows from these data (Fig. 1, curves *3–5*), the conversion of butane over the pressure range 80–190 atm remained constant during the entire experiment and almost complete conversion of the parent hydrocarbon took place. A decrease in the pressure to 40 (curve *2*) or 23 atm (curve *1*) resulted in not only a decrease in the

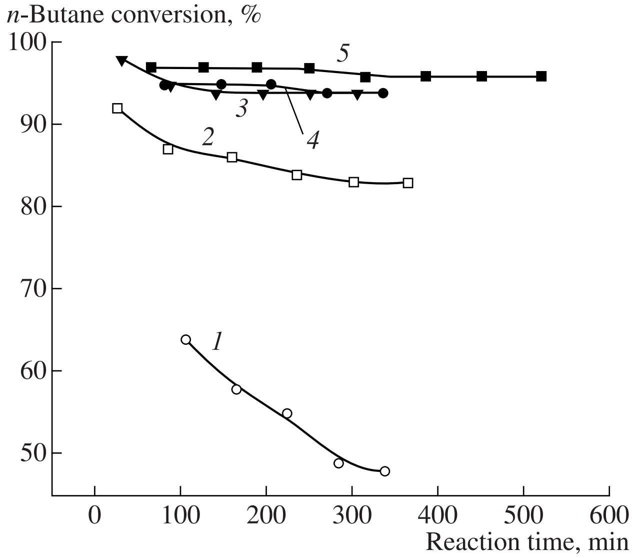


Fig. 1. Conversion of *n*-butane on 2% GaHZSM-5 at 530°C, a butane LHSV of 30 h^{-1}, and P = (*1*) 23, (*2*) 40, (*3*) 80, (*4*) 140, or (*5*) 190 atm.

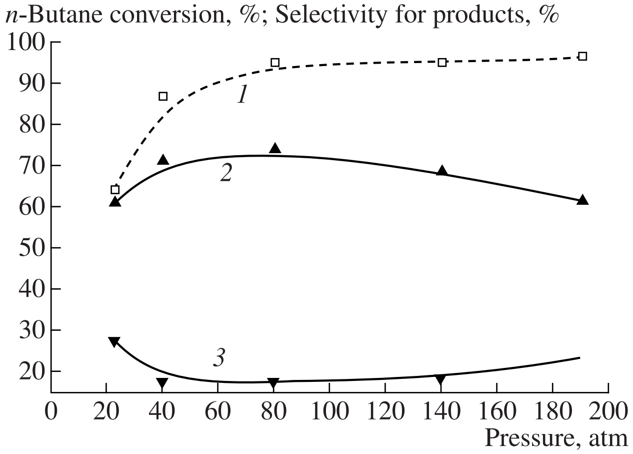


Fig. 2. The pressure dependence of (*1*) *n*-butane conversion on the 2% GaHZSM-5(50) catalyst and selectivity for (*2*) gaseous C_1–iso-C_4 products and (*3*) BTX at 530°C and LHSV = 30 h^{-1}.

initial butane conversion but also catalyst deactivation with time. This is consistent with the fact that both the starting substrate and the reaction products occurred in a gaseous state at 530°C and a pressure lower than 40–50 atm. However, a change to supercritical conditions increased the efficiency of dissolution of the condensation products and, consequently, decreased catalyst deactivation.

Figure 2 shows the pressure dependence of selectivity for various products and the overall conversion of *n*-butane. The selectivity for a BTX fraction decreased from 23 to 17% as the pressure was decreased from 190 to 40 atm. In this case, the total yield of aromatic compounds decreased from 33 to 23%. On the contrary, the selectivity of formation of C_5–C_8 aliphatic hydrocarbons somewhat increased on going from supercritical butane to the gas phase.

A maximum selectivity for gaseous products and a minimum selectivity for BTX, as well as a rapid increase in butane conversion (dashed curve), took place over the pressure range 40–80 atm. At higher pressures, the curve of butane conversion flattened out approaching 95%. Thus, the most pronounced changes in conversion and selectivity for BTX were observed in the transition region between gaseous and supercritical conditions.

The yield of aromatic hydrocarbons dramatically decreased as the pressure of gaseous butane was increased from atmospheric pressure to 40 atm; this is consistent with the process thermodynamics. Indeed, in this case, 40% hydrogen contained in the parent butane was released into the gas phase; this hydrogen shifted the reaction equilibrium of aromatization to the left in accordance with Le Chatelier's principle. The insignificant increase in the yield of aromatic hydrocarbons as the pressure was increased above 80 atm can be due to the suppression of the cracking of aliphatic hydrocarbons at high pressures and the corresponding decrease in the yield of C_1–C_3 gas products. Thus, the results obtained in the study of *n*-butane aromatization in the gas phase and under supercritical conditions suggest different mechanisms of catalytic processes. Table 1 summarizes in more detail the conversion and selectivity for the main reaction products on Ga- and Pt-promoted HZSM-5 zeolite.

These results indicate that the modification of HZSM-5 zeolite with a modulus of 50 with gallium and platinum exerted different effects on the activity and selectivity of the process. Thus, at atmospheric pressure, 530°C, and a butane gas hourly space velocity (GHSV) of 400 h^{-1}, almost complete butane conversion on a catalyst containing 2% gallium was observed at the initial point in time. At the same time, the conversion on a catalyst containing 0.5% platinum was much lower and equal to only 65%. The reaction product distributions on these catalysts were also significantly different from each other. The aromatization of *n*-butane with selectivity for BTX higher than 50% was the main direction of the process at a low pressure in the presence of GaHZSM-5 and ZnHZSM-5 catalysts, whereas cracking and oligomerization reactions were predominant on the platinum-modified zeolite (in this case, the selectivity of formation of C_1–C_3 hydrocarbons was 74–85% and the selectivity for C_{5+} hydrocarbons was up to 5%). Under these conditions, the total selectivity of aromatic hydrocarbon formation was no higher than 20%.

The activity of modified zeolites was high in the reaction performed in supercritical butane at 530°C, 190 atm, and a butane liquid hourly space velocity (LHSV) of 30 h^{-1}. In this case, unlike the gas-phase

Table 1. Conversion of gaseous and supercritical *n*-butane on modified zeolite catalysts at 530°C

Reaction conditions	Reaction time, min	Conversion, %	Selectivity, %				
			C_1–C_3, iso-C_4	C_5–C_8	BTX	C_{9+}	total aromatic hydrocarbons
2% GaHZSM-5(50); gas phase (1 atm; butane GHSV = 400 h^{-1})	15	98	34.3	0.3	52.5	12.9	65.4
	75	95	34.3	0.2	50.3	15.2	65.5
	135	91	38.0	0.4	52.9	8.7	61.6
	195	88	38.4	0.6	52.5	8.5	61.0
	255	82	40.5	0.7	51.2	7.6	58.7
	320	86	39.6	0.6	52.3	7.5	59.9
0.5% PtHZSM-5; gas phase (1 atm; butane GHSV = 400 h^{-1})	30	65	74.0	2.8	19.8	3.4	23.2
	90	53	78.4	4.1	15.0	2.4	17.4
	160	45	81.3	4.4	12.4	1.8	14.2
	220	42	82.3	4.7	11.3	1.7	13.0
	275	40	83.0	4.8	10.6	1.5	12.2
	340	37	84.2	4.8	9.7	1.3	11.0
2% GaHZSM-5(50); supercritical conditions (190 atm; butane LHSV = 30 h^{-1})	0	98	63.3	0.6	21.6	14.5	36.0
	65	97	61.5	1.0	23.2	14.3	37.5
	125	97	62.6	1.0	22.8	13.6	36.3
	190	97	64.5	1.3	22.2	11.9	34.1
	250	97	64.7	1.5	22.3	11.6	33.9
	315	96	65.4	1.6	22.0	11.1	33.1
	385	96	65.3	1.7	22.1	10.9	33.0
	450	96	65.7	1.8	22.1	10.4	32.5
	520	96	65.8	2.0	22.1	10.1	32.2
0.5% PtHZSM-5(50); supercritical conditions (190 atm; butane LHSV = 30 h^{-1})	90	99	63.6	0.3	23.0	13.1	36.1
	150	99	62.1	0.3	23.0	14.6	37.6
	205	99	62.1	0.3	23.2	14.4	37.6
	260	99	60.9	0.5	23.3	15.2	38.5
	320	99	63.2	0.6	23.0	13.2	36.2

reactions performed on the catalysts modified with Ga, Zn, and Pt, there was almost no difference in product distributions. The selectivity for BTX was 21–23%, and the total amount of aromatic hydrocarbons was as high as 40%. Gaseous reaction products accounted for 60–65%.

The distribution of alkanes and alkenes in cracking gas also depended on process conditions (Table 2).

Thus, the greatest amount of olefins (ethylene and propylene) was formed in the case of a gas-phase reaction. In this case, the ratio of the sum of methane, ethane, and propane to the sum of ethylene and propylene was equal to 3 or 10 on the 0.5% PtHZSM-5 or 2% Ga/HZSM-5 catalyst, respectively; this suggests that the dehydrogenating capacity of platinum is higher than that of gallium. Ethylene and propylene were practically not formed in the reaction performed on modified pentasils under supercritical conditions.

Note that catalysts based on modified pentasils are prone to deactivation under gas-phase reaction conditions at 530°C. On the contrary, butane conversion was close to 100% under supercritical conditions, and it did not decrease in the course of the reaction for 8–10 h. In addition, note that the conversion of supercritical butane occurred at an LHSV of 30 h^{-1}, whereas the LHSV of butane under gas-phase conditions was as low as 1.8 h^{-1}, which corresponds to a butane GHSV of

Table 2. Selectivity for saturated and unsaturated C_1–C_3 products from n-C_4H_{10} in the gas phase and under supercritical conditions at 530°C

Catalyst	P, atm	Space velocity, h^{-1}	Selectivity, %					$\frac{CH_4 + C_2H_6 + C_3H_8}{C_2H_4 + C_3H_6}$ ratio
			CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	
2% Ga/HZSM-5(50)	1	1.8	28.9	27.2	5.1	34.6	4.2	10
	1		35.7	25.3	4.9	30.6	3.5	11
0.5% Pt/HZSM-5(50)	1	1.8	10.2	27.0	14.7	35.5	12.6	3
	1		11.8	28.4	15.4	34.4	10.0	3
2% Ga/HZSM-5(50)	190	30	13.6	23.1	0.5	62.5	0.3	124

400 h^{-1}. Therefore, the substrate-to-catalyst ratio under supercritical conditions was higher than the corresponding value for the gas-phase reaction by a factor of almost 20.

Figure 3 compares the catalyst performance at atmospheric pressure and under supercritical conditions as the dependence of the overall conversion of n-butane on the amount of n-butane passed through the catalyst in the course of reaction. Curve *1* for butane conversion on GaHZSM-5 clearly demonstrates the advantages of the process performed under supercritical conditions: the conversion of butane was stable on supplying 2–3 mol per 1 cm^3 of the catalyst. On the contrary, the deactivation of Zn- and Ga-containing zeolites in the gas-phase reaction (curves *2*, *3*) occurred at butane loadings of 0.1–0.15 mol per 1 cm^3 of the catalyst. Thus, the operational efficiency of aromatization catalysts under supercritical conditions in terms of activity, productivity, and resistance to poisoning by condensation products is much higher than the corresponding parameters of the reaction performed in the gas phase.

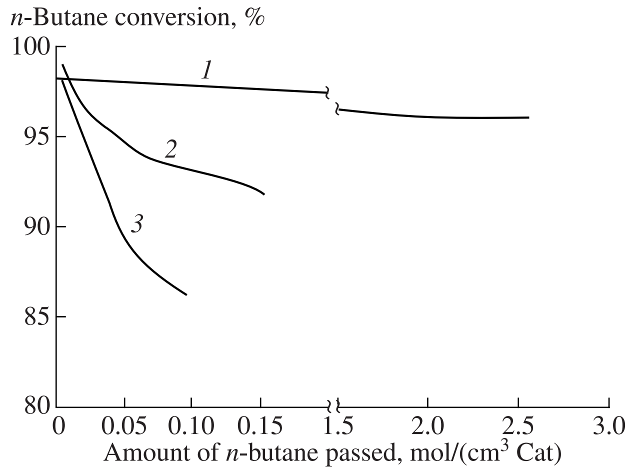


Fig. 3. n-Butane conversion on modified pentasils: (*1*) supercritical conditions, T = 530°C, P = 190 atm, LHSV = 30 h^{-1}, 2% GaHZSM catalyst; (*2*) gas phase, T = 530°C, P = 1 atm, LHSV = 1.8 h^{-1}, 2% ZnHZSM-5 catalyst; (*3*) the above conditions, 2% GaHZSM-5 catalyst.

We studied the poisoning of aromatization catalysts in the course of reaction using thermogravimetry. Figure 4 shows the thermal analysis curves obtained by the temperature-programmed oxidation of a 2% GaHZSM-5(50) catalyst after 8.5-h operation under supercritical conditions at 530°C and 190 atm. Qualitatively, the shapes of DTA–TG curves for the catalysts exposed both under supercritical conditions and in the gas phase were similar; this fact suggests that the same condensation product species formed on the catalyst surfaces caused catalyst deactivation. In both cases, the positions of extremums in the curves were also identical. However, peak intensities strongly differed from each other. This is indicative of different amounts of coke precursors depending on operating conditions. Table 3 summarizes the corresponding quantitative thermal analysis data.

In the gas-phase reactions of butane performed for 5.5 and 8.5 h on Ga/HZSM-5 and Zn/HZSM-5 catalysts, the total coke deposition was 6.5 and 8.0% on a sample weight basis, respectively. In this case, 2/3 of the total weight loss in these catalysts was observed to ~275°C, and the other third of coke deposits was burnt off at the second stage. The removal of coke came into play at about 470°C with a maximum temperature of 528–530°C. Thus, the shapes of DTA curves for catalysts operated under gas-phase reaction conditions

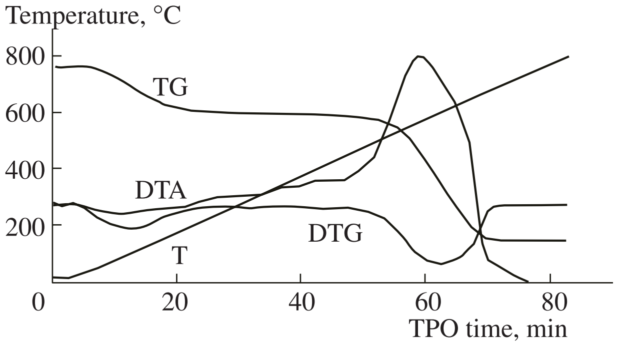


Fig. 4. Thermal analysis curves for the 2% GaHZSM-5 catalyst after supercritical butane conversion at T = 530°C, P = 190 atm, and a butane LHSV of 30 h^{-1} for 8.5 h.

Table 3. TG–DTA data for catalysts deactivated under various reaction conditions

No.	Reaction conditions	Weight loss, %			$T_{\max}$, °C	
		total	stage 1	stage 2	DTG curve	DTA curve
1	2% Ga/HZSM-5; gas phase (530°C; 1 atm; 5.5 h)	6.5	4	2	69–87, 531–552	endo 71–73, exo 528–530 (onset at 470)
2	2% Zn/HZSM-5; gas phase (530°C; 1 atm; 8.5 h)	8.0	5.2	2.4	71–75, 525–530	endo 81–82, exo 515–518 (onset at 455)
3	2% Ga/HZSM-5; supercritical conditions (530°C; 190 atm; 8.5 h)	23.9	3.6	19.7	70, 84–119; 601–636	endo 59–71, exo 545–549 in the range ~419–690
4	0.5% Pt/HZSM-5; supercritical conditions (530°C; 190 atm; 5.5 h)	31.1	4.7	26.3	111–113, (257–261) (618–642) 689–690	endo 85–88, exo 262–263, 370–373, 552–555, 705

reflect the inhomogeneous character of condensation products. These results are consistent with data published by Yakerson et al. [9], who found that condensation products formed in the course of propane aromatization on pentasils modified with zinc and gallium are aromatic compounds localized both in channels and on the outer surfaces of the catalysts.

After the reactions performed in supercritical butane at 530°C and 190 atm on Ga/HZSM-5 and Pt/HZSM-5 catalysts for 5.5–8.5 h, a two-stage weight loss was also observed in the course of linear heating to 800°C in air. The first endothermic effect was characterized by a weight loss of only ~3–5%. The second endothermic effect related to the removal of coke deposits came into play at ~420°C (a maximum temperature of ~545°C). In this case, the total weight loss was about 20–27%.

Although, unlike the gas-phase reaction, the weight of total condensation products after operation under supercritical conditions was equal to about a third of the weight of the spent catalyst, this was not accompanied by a noticeable change in the catalyst activity. Butane conversion was retained at a level of 95%, and the total amount of converted butane was greater than that in the gas-phase reaction by a factor of 20. The total amount of condensation products deposited on catalysts in the supercritical experiment was higher than that in the gas-phase experiment by a factor of 3–4. Evidently, a supercritical fluid efficiently eliminates only low-temperature condensation products and cannot dissolve coke, which is burnt off at temperatures higher than 500°C.

ACKNOWLEDGMENTS

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REFERENCES

1. Minachev, Kh.M. and Dergachev, A.A., *Itogi Nauki Tekh., Ser.: Kinet. Katal.*, 1990, vol. 23, p. 3.
2. Minachev, Kh.M. and Dergachev, A.A., *Usp. Khim.*, 1990, vol. 59, no. 9, p. 1522.
3. US Patent 5043502, 1991.
4. Bogdan, V.I., Klimenko, T.A., Kustov, L.M., and Kazanskii, V.B., *Kinet. Katal.*, 2004, vol. 45, no. 6, p. 942 [*Kinet. Catal.* (Engl. Transl.), vol. 45, no. 6, p. 890].
5. Bogdan, V.I., Klimenko, T.A., Kustov, L.M., and Kazansky, V.B., *Appl. Catal., A*, 2004, vol. 267, p. 175.
6. Bogdan, V.I. and Kazanskii, V.B., *Katal. Prom–sti.*, 2005, no. 3, p. 43.
7. Bogdan, V.I. and Kazanskii, V.B., *Kinet. Katal.*, 2005, vol. 46, no. 6, p. 881 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 6, p. 834].
8. Reid, R., Prausnitz, J., and Sherwood, T., *The Properties of Gases and Liquids*, New York: McGraw-Hill, 1977.
9. Yakerson, V.I., Vasina, T.V., Bragin, O.V., Sitnik, V.P., Nissenbaum, V.D., Lafer, L.I., Denisova, E.L., and Dykh, Zh.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, no. 9, p. 1962.