ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 3, pp. 410–415. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.E. Koklin, V.M.Kh. Chan, V.B. Kazanskii, V.I. Bogdan, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 3, pp. 429–434.

# Alkylation of Isobutane with $C_4$ Olefins under Conventional and Supercritical Conditions

**A. E. Koklin, V. M. Kh. Chan, V. B. Kazanskii, and V. I. Bogdan**

*Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

*e-mail: akok@yandex.ru*

Received April 8, 2009

**Abstract**—The solid acid alkylation of isobutane with butylenes on the ultrastable zeolite Y is studied in the temperature range from 120 to 150°C and in a pressure range of 20–120 atm. The catalyst service life becomes longer on passing from the conventional (liquid- and gas-phase) conditions of alkylation to supercritical conditions. The maximum period of complete butylene conversion at 150°C and 120 atm is 3.5 h. The composition of the reaction products is determined by the phase state of the reaction mixture, the reaction time, and the conversion of the $C_4$ olefins. When the alkylation is carried out under supercritical conditions, the $C_8$ hydrocarbon selectivity varies between 30 and 40%. Thermoanalytical data suggest that the surface of the spent catalyst contains carbon deposits indicating the formation of oligomeric and cyclic structures.

**DOI:** 10.1134/S0023158410030146

Isobutane alkylation with butylenes is an ideal process for the production of components of modern, environmentally friendly gasoline due to the alkylate having a high octane number, low saturated vapor pressure, and low sulfur and aromatic and unsaturated hydrocarbon contents. Concentrated sulfuric and hydrofluoric acids are presently used as industrial catalysts for this process [1]. Liquid acid alkylation has significant drawbacks, namely, the high toxicity and corrosion activity of these mineral acids. Solution of the environmental problems of alkylate production and reduction of the capital costs and safety expenses are possible by passing to solid acid alkylation catalysts [2, 3]. However, the main difficulty in the practical use of these catalysts is associated with their fast deactivation [3, 4].

At present, many researchers are greatly interested in performing catalytic processes under unconventional conditions. One of the possible approaches to the problem of the poisoning of the alkylation catalyst is to conduct this reaction under supercritical conditions [5–7]. As was shown by many studies, supercritical fluids can dissolve condensation products resulting from side reactions and can remove them from the catalyst surface. This regenerates the heterogeneous catalyst and extends its service life [8, 9].

The purpose of the present work is to compare the catalytic activities, selectivities, and service lives of zeolite Y in the alkylation of isobutane with butylenes under supercritical and conventional (liquid- and gas-phase) conditions.

## EXPERIMENTAL

The H-forms of zeolite Y with $SiO_2/Al_2O_3$ ratios of 5.5 and 10.5 (hereafter, HY-5.5 and HY-10.5) obtained by the thermal decomposition of the $NH_4$-forms were used as catalysts for isobutane alkylation. The starting powder catalysts were pressed into pellets and crushed, and the 0.25–0.42 mm particle size fraction was taken. Prior to experiments, the zeolites were calcined in a dry air flow at 500°C for 3 h. The volume of a catalyst loaded into the reactor was 1 or 2 $cm^3$. The feed was a mixture of isobutane with butylenes (Table 1). The total concentration of butenes (but-1-ene, isobutene, *trans*-but-2-ene, *cis*-but-2-ene) in the initial mixture was 6.2 wt %. The isobutane : $C_4$ olefins molar ratio was 16 : 1. This mixture was prepared by diluting the mixture of $C_4$ hydrocarbons with neat isobutane.

The alkylation reaction was studied at temperatures from 120 to 150°C in the pressure range 20–120 atm. Catalytic experiments were carried out in a U-shaped flow reactor. The catalyst was heated to the

**Table 1.** Initial composition of the isobutane–butylene mixture

| Component | Concentration, wt % |
|---|---|
| Isobutane | 91.8 |
| Isobutene + but-1-ene | 3.5 |
| *n*-Butane | 2.0 |
| *trans*-But-2-ene | 1.8 |
| *cis*-But-2-ene | 0.9 |

reaction temperature in a helium flow. The pressure in the system was created by supplying the reaction mixture with a high-pressure liquid displacement pump at a rate of 6 ml/h. The pressure was controlled using a membrane valve. The liquid hourly space velocity of the feed ($V_L$, $cm^3\ h^{-1}\ (cm^3\ Cat)^{-1}$), determined as the ratio of the flow rate of the reactants in the liquid state at 20°C to the catalyst volume, was 3 or 6 $h^{-1}$.

The reaction products were analyzed on a chromatograph equipped with a Thermo TR-5MS capillary column (30 m). Particular samples of the catalyzate were analyzed by gas chromatography coupled with mass spectrometry to identify its components. Since isobutane and butylenes were not completely separated in the TR-5MS column, they were analyzed on another chromatograph using a capillary column with the supported OV-101 phase (100 m). The concentration of butylenes was calculated from the thus-obtained quantitative ratio of $C_4$ hydrocarbons.

The conversion of butylenes ($X$) and the selectivity ($S$) for the $C_5$–$C_7$, $C_8$, and $C_{9+}$ hydrocarbon groups were calculated using the following formulas:

$$X = (c - c')/c \times 100\%, \quad (1)$$

$$S(i) = \sum_i c(i) \Big/ \sum_k c(k) \times 100\%, \quad (2)$$

where $c$ and $c'$ are the initial and final total concentrations of all butanes and $\sum_i c(i)$ and $\sum_k c(k)$ are the total concentration of the hydrocarbons from a particular group and the total concentration of all reaction products, respectively.

The amount of condensation products on spent catalysts was determined by thermogravimetry using an STA 449PC Jupiter thermal analyzer (Netzsch) with simultaneous mass spectrometric analysis of the gaseous products formed upon heating of the samples. The measurements were carried out under linear-law heating at a rate of 5 K/min in an argon flow (60 ml/min).

The pseudocritical parameters of the mixture were calculated using the empirical rules given below [10]. If the $0.5 < T_{c,i}/T_{c,j} < 2$ and $0.5 < P_{c,i}/P_{c,j} < 2$ conditions are fulfilled for any mixture components $i$ and $j$, the pseudocritical temperature of the mixture can be determined with a sufficient accuracy (the deviation is less than 2%) according to Kay's rule

$$T_{c,mix} = \sum_i x_i T_{c,i}, \quad (3)$$

where $T_{c,i}$ and $x_i$ are the critical temperature and molar fraction of the $i$th component of the mixture, respectively. Acceptable pseudocritical pressures for mixtures consisting of similar components are given by the modified Prausnitz–Hann rule

$$P_{c,mix} = \frac{R\left(\sum_i x_i Z_{c,i} T_{c,mix}\right)}{\sum_i x_i V_{c,i}}, \quad (4)$$

where $Z_{c,i}$ and $V_{c,i}$ are the compressibility factor and molar volume of the component $i$ at $T_c$ and $P_c$, respectively.

The pseudocritical parameters of the initial reaction mixture of $C_4$ hydrocarbons calculated by formulas (3) and (4) using the data in Table 2 are 135.5°C and 35.7 atm.

**Table 2.** Critical parameters for $C_4$ hydrocarbons [10]

| Compound | $T_c$, °C | $P_c$, atm | $Z_c$ | $V_c$, ml/mol |
|---|---|---|---|---|
| *n*-Butane | 152.2 | 37.5 | 0.274 | 255 |
| Isobutane | 135.1 | 36.0 | 0.274 | 263 |
| But-1-ene | 146.6 | 39.7 | 0.277 | 240 |
| *cis*-But-2-ene | 162.6 | 41.5 | 0.272 | 234 |
| *trans*-But-2-ene | 155.6 | 40.5 | 0.274 | 238 |

## RESULTS AND DISCUSSION

For the comparative study of isobutane alkylation with $C_4$ olefins, we chose the reaction parameters (pressure, temperature, LHSV of the mixture, and catalyst weight) ensuring the complete conversion of

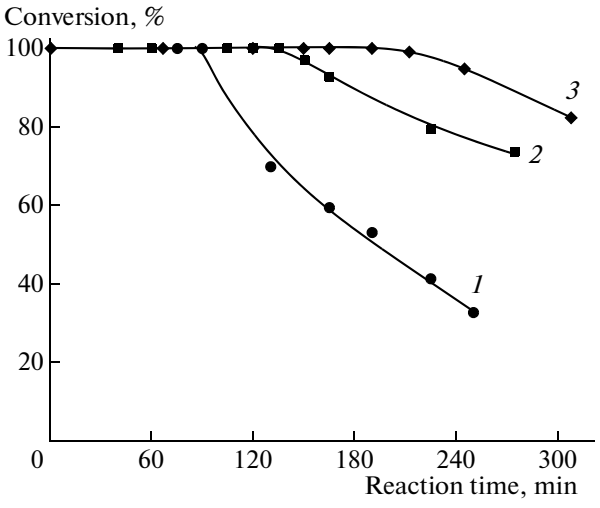


**Fig. 1.** Time variation of the butylene conversion in isobutane alkylation with butylenes on the catalyst HY-10.5 in the gaseous phase at (*1*) $P = 20$ atm and under the supercritical conditions at (*2*) $P = 80$ and (*3*) 120 atm; $T = 150$°C, $V_L = 3\ h^{-1}$.

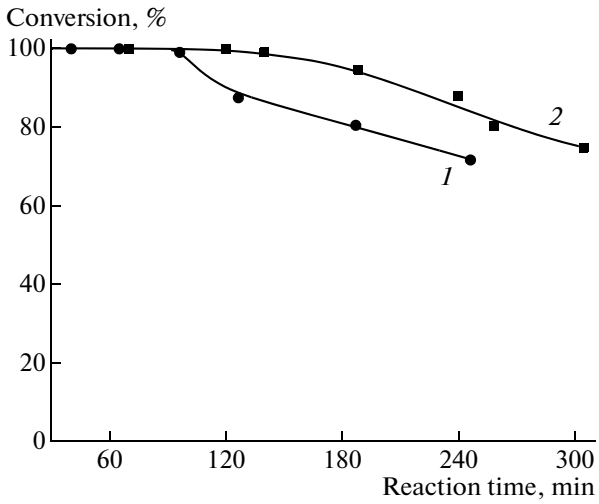


**Fig. 2.** Time variation of the butylene conversion in isobutane alkylation with butylenes on the catalyst HY-10.5 (*1*) in the liquid phase and (*2*) under the supercritical conditions at 80 atm and temperatures of (*1*) 120 and 140°C; $V_L = 3\ h^{-1}$.

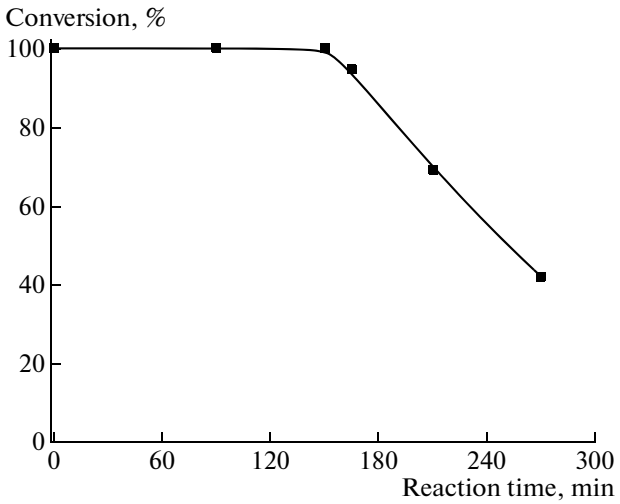


**Fig. 3.** Time variation of the butylene conversion in isobutane alkylation with butylenes on the catalyst HY-5.5 under the supercritical conditions (150°C, 80 atm, $V_L = 3\ h^{-1}$).

butylenes under both conventional (gas-phase, liquid-phase) and supercritical conditions.

Under the gas-phase conditions of alkylation at 150°C and 20 atm, the complete conversion of butylenes on the HY-10-5 catalyst is observed over 90 min. Then the catalyst is deactivated rather rapidly (Fig. 1, curve *1*). According to the above calculations of the parametric state of the mixture of $C_4$ hydrocarbons, raising the pressure to 80 atm brings the reaction mixture into the supercritical state. As can be seen from the data presented in Fig. 1 (curve *2*), alkylation under the supercritical conditions increases the interval of complete conversion of $C_4$ olefins to 140 min and decreases the catalyst deactivation rate. Further raising the pressure to 120 atm also exerts a positive effect on the catalyst service life (Fig. 1, curve *3*).

When the reaction is carried out in the liquid phase, the complete conversion of butylenes is observed over the first 90 min of the reaction, and then their conversion gradually decreases (Fig. 2). On passing to the supercritical conditions, as the temperature increases to 140°C, the period of stable catalyst operation ensuring the 100% conversion of butylenes extends to 140 min.

The selectivity with respect to the isobutane–butylenes mixture conversion products depends, to a considerable extent, on the process conditions. According to the data presented in Table 3, almost no isobutane alkylation and no dimerization of $C_4$ olefins occur under the gas-phase conditions. The $C_8$ hydrocarbon selectivity does not exceed a few percent, and $C_5$–$C_7$ and $C_{9+}$ hydrocarbons are the major conversion products. At the same time, the $C_8$ selectivity reaches ~40% in the liquid phase and under the supercritical conditions. In the initial period of the reaction, when the butylene conversion is 100% (within 30–190 min, depending on the conditions), the major $C_8$ hydrocarbons are isooctanes, while the fraction of octenes is lower than 5% (Table 3). Both trimethylpentanes (products of direct alkylation) and less branched dimethylhexanes and methylheptanes are observed among the isooctanes. The fraction of methylheptanes in the $C_8$ alkanes is low (5–18%) and gradually decreases during the reaction down to complete disappearance. The ratio of trimethylpentanes to dimethylheptanes upon the alkylation under the supercritical conditions is 0.6–0.8, and in the liquid phase it decreases from 1.4 to 0.7 as the catalyst is deactivated.

The time dependence of the butylene conversion under the supercritical conditions on zeolite HY-5.5 is presented in Fig. 3. Figures 1 and 3 show that the period of the stable operation of the catalysts HY-5.5 and HY-10.5 in isobutane alkylation at 150°C and 80 atm is ~140 min. It can be assumed that the rather high concentration of strong Brønsted acid sites necessary for isobutane activation is retained as the $SiO_2/Al_2O_3$ ratio in the zeolite is increased from 5.5 to 10.5. The dominant removal of weak and medium-strength acid sites at the 50% dealumination of zeolites Y was observed [11].

As follows from the results presented here, the service life of the catalyst lengthens on passing to the supercritical alkylation conditions. The dissolving properties of supercritical isobutane favor the removal of the precursors of condensation products from the catalyst surface, decreasing the rate of formation of heavy oligomers and coke [12]. The value of the $C_8$ hydrocarbon selectivity (30–40%, Table 3) for alkylation under the supercritical conditions is consistent with earlier data. For the alkylation of isobutane with

**Table 3.** Products of isobutane alkylation with butylenes on HY-10.5 under conventional and supercritical conditions

| Time, min | Conversion, % | Selectivity, % | | | Distribution of $C_8$ hydrocarbons, % | | | Distribution of $C_8$ alkanes**, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_5$–$C_7$ | $C_8$ | $C_{9+}$ | alkanes | olefins | naphthenes | $MC_7$ | DMH | TMP |
| Gaseous phase | | | | | | | | | | |
| 150°C, 20 atm* | | | | | | | | | | |
| 30 | 100 | 60 | <1 | 40 | 41 | 59 | 0 | – | – | – |
| 215 | 43 | 16 | 2 | 83 | 27 | 73 | 0 | – | – | – |
| Liquid phase | | | | | | | | | | |
| 120°C, 80 atm* | | | | | | | | | | |
| 30 | 100 | 44 | 38 | 18 | 99 | 1 | 0 | 5 | 40 | 55 |
| 70 | 100 | 12 | 35 | 53 | 79 | 21 | 0 | 3 | 57 | 40 |
| 245 | 72 | 6 | 37 | 56 | 33 | 67 | 0 | 0 | 60 | 40 |
| Supercritical conditions | | | | | | | | | | |
| 140°C, 80 atm* | | | | | | | | | | |
| 45 | 100 | 49 | 34 | 17 | 98 | 1 | 1 | 13 | 49 | 38 |
| 145 | 98 | 19 | 39 | 43 | 80 | 20 | 0 | 3 | 58 | 38 |
| 240 | 85 | 7 | 37 | 56 | 39 | 61 | 0 | 0 | 62 | 38 |
| 150°C, 80 atm* | | | | | | | | | | |
| 45 | 100 | 37 | 32 | 30 | 96 | 2 | 2 | 16 | 54 | 30 |
| 175 | 90 | 17 | 39 | 43 | 60 | 40 | 0 | 0 | 61 | 39 |
| 150°C, 120 atm* | | | | | | | | | | |
| 60 | 100 | 58 | 31 | 11 | 95 | 4 | 0 | 18 | 47 | 35 |
| 190 | 100 | 25 | 33 | 42 | 99 | 0 | 0 | 10 | 58 | 32 |
| 290 | 86 | 12 | 37 | 51 | 44 | 56 | 0 | 0 | 63 | 37 |

* $V_L = 3\ h^{-1}$; ** $MC_7$ = methylheptanes, DMH = dimethylhexanes, and TMP = trimethylpentanes.

**Table 4.** Products of isobutane alkylation with butylenes on HY-10.5 under the supercritical conditions at 150°C, 80 atm, and $V_L = 6\ h^{-1}$

| Time, min | Period | Selectivity, % | | | Distribution of $C_8$ hydrocarbons, % | | | Distribution of $C_8$ alkanes*, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_5$–$C_7$ | $C_8$ | $C_{9+}$ | alkanes | olefins | naphthenes | $MC_7$ | DMH | TMP |
| 50 | I | 22 | 31 | 47 | 99 | 1 | 0 | 8 | 55 | 37 |
| 150 | II | 17 | 45 | 37 | 36 | 64 | 0 | 0 | 59 | 41 |
| 230 | III | 5 | 87 | 8 | 4 | 96 | 0 | 0 | 87 | 13 |

* For designations, see Table 3.

butylenes on zeolites Beta and Y under supercritical conditions, the $C_8$ selectivity is 50–55% [6]. In the latter case, the higher selectivity is due to the use of a very low concentration of $C_4$ olefins in the reaction mixture (isobutane/butylenes = 107), resulting in a decrease in the probability of their oligomerization. A selectivity close to 80% can be achieved by carrying out the process in the liquid phase at low temperatures of 40–80°C, when the rate of the side cracking reaction is insignificant. However, the catalyst is deactivated rather rapidly [3, 13, 14]. It was shown [14] that at 40°C the butylene conversion on the catalyst H-USY in the first hour of the reaction decreases from 100% to 35% with a simultaneous decrease in the alkylation selectivity from 80 to 30%.

The results of isobutane alkylation with butylenes under the supercritical conditions at different $V_L$ values are shown in Fig. 4. The period of complete butylene conversion shortens as $V_L$ is raised. The $C_5$–$C_7$ selectivity and the fraction of methylheptanes among the resulting isooctanes also decrease (Tables 3, 4).

By analogy to the earlier reported division of the conversion curve into several portions [3], the operation of the catalyst HY in the alkylation of isobutane

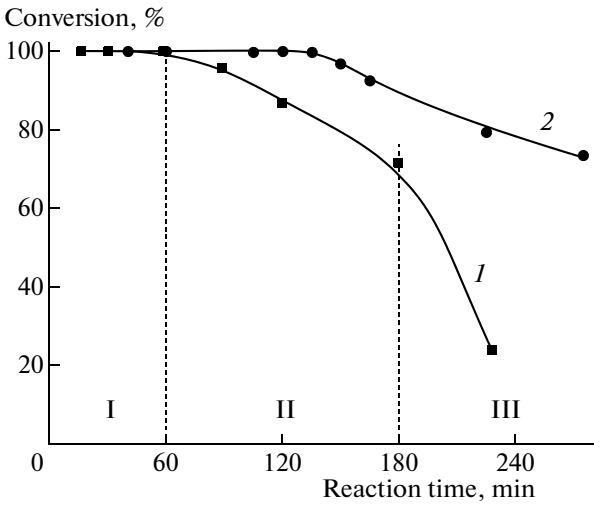


**Fig. 4.** Time variation of the butylene conversion in isobutane alkylation with butylenes on the catalyst HY-10.5 under the supercritical conditions at 150°C, 80 atm, and $V_L$ = (*1*) 6 and (*2*) 3 $h^{-1}$.

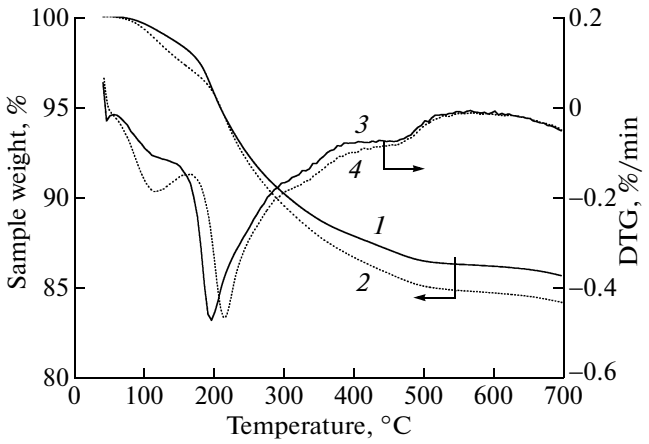


**Fig. 5.** Thermogravimetric analysis of the catalyst HY-5.5 after the alkylation reaction under the supercritical conditions (150°C, 80 atm, $V_L$ = 3 $h^{-1}$). The reaction time is (*1, 3*) 165 and (*2, 4*) 270 min. DTG is the rate of weight change upon heating of the sample.

with butylenes under the supercritical conditions can be divided into three periods. This division is clearly seen when $V_L$ is increased from 3 to 6 $h^{-1}$ (Fig. 4). The alkylation of isobutane with butylenes prevails in the first period, whereas the formation of $C_8$ olefins is insignificant. Oligomerization/cracking processes occur in parallel with alkylation, affording considerable amounts of $C_5$–$C_7$ and $C_{9+}$ by-products. In the second period, the catalytic activity begins to decrease. The dimerization of $C_4$ olefins occurs, resulting in an increase in the fraction of octenes in the $C_8$ hydrocarbons. In the third period, the catalytic activity decreases rather rapidly, which is probably due to the domination of the oligomerization reaction. The $C_8$ selectivity exceeds 85%, and 90% of the $C_8$ products are olefins (Table 4). It is likely that the accumulation rate of the oligomeric products on the zeolite surface and in the pores is higher than the rate of their dissolution and removal from the catalyst. These processes eventually lead to catalyst deactivation even under supercritical conditions.

After the reaction under the supercritical conditions, several samples of the catalyst HY-5.5 were studied by thermogravimetry to determine the degree of coking and to identify the condensation products. The composition of the carbon deposits on the catalyst surface was determined from the mass spectra of gaseous substances formed u8pon heating of these samples. The thermogravimetric data for HY-5.5 after 165- and 270-min-long runs are shown in Fig. 5. Note that the butylene conversion on these samples had decreased to that moment from 100 to 95 and 42%, respectively. During heating in a He flow, both samples lose weight in several steps. The first step ($T$ < 300°C) corresponds to the thermal desorption of the oligomerization products; i.e., only the signals corresponding to the aliphatic hydrocarbon fragments are detected by mass spectrometry. The observed shift of the DTG peak at 200°C (Fig. 5) to higher temperatures possibly indicates the formation of heavier oligomeric condensation products or an increase in the degree of their unsaturation (decrease in the C : H ratio) with an increase in the reaction time. In the second step of the weight loss, which occurs in the temperature interval from 300 to 560°C, the mass spectrum of the thermal desorption products shows signals assignable to ions containing a benzene ring. This fact indicates the cyclization of polyene compounds adsorbed on the catalyst surface.

**Table 5.** Degree of coking of the HY-5.5 samples after the alkylation of isobutane with butylenes under the supercritical conditions (150°C, 80 atm, 3 $h^{-1}$)

| Desorption temperature, °C | Weight loss of sample, wt % | |
|---|---|---|
| | reaction time of 165 min | reaction time of 270 min |
| 40–300 | 9.8 | 10.6 |
| 300–560 | 3.9 | 4.7 |
| Total | 13.7 | 15.3 |

The stepped weight loss shown by the samples during thermal analysis is due to the presence of the condensation products of two different types—oligomeric and cyclic structures—on the surface of the spent catalysts. The data in Table 5 show that an increase in the exposure time is accompanied by an increase in the amount of condensation products on the catalyst surface and in the amount of the removed carbon deposits at each stage of thermal desorption. The composition of the condensation products changes insignificantly.

The data obtained in this study are consistent with the mechanism of deactivation of the alkylation catalysts [3, 15]. The formation and accumulation of polydienes and related compounds followed by their cyclization into highly stable cyclopentadienyl and aromatic structures on the surface of the catalysts HY are the main causes of their deactivation under the supercritical conditions.

Thus, as was shown by the study of the alkylation of isobutane with butylenes on ultrastable zeolite Y, the service life of the catalyst under the supercritical conditions is longer than that of the same catalyst under gas–liquid conditions. The $C_8$ hydrocarbon selectivity in alkylation under the supercritical conditions is 30–40%. At the early stages of the reaction, the fraction of octane isomers in the $C_8$ products reaches 100%, and it decreases with catalyst deactivation. The time during which butylenes are converted completely can be extended by raising the pressure.

## ACKNOWLEDGMENTS

The authors are grateful to Chevron Energy Technology Company for financial support and for kindly presented catalyst samples. This study was supported by the Presidium of the Russian Academy of Sciences (Basic Research Program no. 18), President of the Russian Federation (Leading Scientific School Program no. NSh-5746.2006.3), and the Russian Foundation for Basic Research (project no. 07-03-00299-a).

## REFERENCES

1. Smidovich, E.V., *Tekhnologiya pererabotki nefti i gaza* (Oil and Gas Processing Technology), Moscow: Khimiya, 1986, part 2.
2. Corma, A. and Martinez, A., *Catal. Rev. Sci. Eng.*, 1993, vol. 35, no. 4, p. 483.
3. Lavrenov, A.V., Bogdanets, E.N., and Duplyakin, V.K., *Katal. Prom–sti.*, 2009, no. 1, p. 28.
4. Querini, C.A. and Roa, E., *Appl. Catal., A*, 1997, vol. 163, p. 199.
5. 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].
6. Mota Salinas, A.L., Sapaly, G., Ben Taarit, Y., Vedrine, J.C., and Essayem, N., *Appl. Catal., A*, 2008, vol. 336, nos. 1–2, p. 61.
7. Clark, C.M. and Subramaniam, B., *Ind. Eng. Chem. Res.*, 1998, vol. 37, no. 4, p. 1243.
8. Ginosar, D.M., Thompson, D.N., and Burch, K.C., *Appl. Catal., A*, 2004, vol. 262, no. 2, p. 223.
9. Baiker, A., *Chem. Rev.*, 1999, vol. 99, no. 2, p. 453.
10. Reid, R., Prausnitz, J., and Sherwood, T., *The Properties of Gases and Liquids*, New York: McGraw-Hill, 1977.
11. Mishin, I.V., Klyachko, A.L., Brueva, T.R., Tkachenko, O.P., and Baier, G.-K., *Kinet. Katal.*, 1993, vol. 34, no. 3, p. 565.
12. Thompson, D.N., Ginosar, D.M., and Burch, K.C., *Appl. Catal., A*, 2005, vol. 279, nos. 1–2, p. 109.
13. Querini, C.A. and Roa, E., *Appl. Catal., A*, 1997, vol. 163, nos. 1–2, p. 199.
14. Mota, C.J.A. and Rosenbach, N.J., *J. Braz. Chem. Soc.*, 2005, vol. 16, no. 4, p. 691.
15. Feller, A., Zuazo, I., Guzman, A., Barth, J.O., and Lercher, J.A., *J. Catal.*, 2003, vol. 216, nos. 1–2, p. 313.