Oligomerization of Butenes on Borate-Containing Alumina

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Abstract—The effects of the chemical composition of borate-containing alumina on its physicochemical properties, catalytic activity, and selectivity in the oligomerization of butenes are reported. The preparation of catalysts containing 2.6–12.4 wt % B_2O_3 by modifying γ-alumina with orthoboric acid leads to a 9–60 m^2/g decrease in the specific surface area and to a 0.02–0.14 cm^3/g decrease in the pore volume relative to the same parameters of the initial support. At boron oxide contents of ≥8.8 wt %, these changes are due to the buildup of B_2O_3 on the catalyst surface. This is accompanied by a decrease in the number of surface B–OH groups, which are active sites of oligomerization. This finding correlates well with the results of catalytic measurements. The catalyst containing 4.5 wt % B_2O_3 is the most active. It was found by experimental design methods that the most favorable combination of catalytic activity (total butene conversion of 77.8–86.8%) and selectivity (butene oligomer concentration of at least 90 wt % in the liquid product) is attained at $T = 150°C$, $P = 8.0$ MPa, and a butene WHSV of 0.5–1.0 h^{-1}. Under these conditions, the butene conversion decreases by no more than 13% from the initial level in 14 h. The activity of the catalyst can be restored by oxidative regeneration.

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The oligomerization of butenes has long been known as a way of producing components of high-grade fuels [1]. In view of the recent tightening of environmental standards, it has become advantageous to hydrogenate unsaturated oligomerization products into $C_8–C_{16}$ isoalkanes and to use them as components of antiknock gasoline [2, 3] and jet and diesel fuels [4] for reducing the sulfur and aromatic hydrocarbon contents. The present-day interest in oligomerization is boosted by the possibility of obtaining light alkenes not only by petroleum pyrolysis and cracking, but also by the Fischer–Tropsch processing of natural gas [5] and oxidative pyrolysis [6].

Most commercial-scale butene oligomerization processes use silica–phosphate catalysts (so-called solid phosphoric acid). The fundamental drawbacks of these catalysts are their destruction during operation and the impossibility of their regeneration and reuse [7, 8]. The most promising catalytic systems for oligomerization are sulfonic resins [9–11], amorphous aluminosilicates [12], various zeolites [13–15], and anion-modified metal oxides. Among the latter, sulfated zirconia [16, 17], sulfated titania [18, 19], and tungstate-containing titanium dioxide [17, 20, 21] have attracted the greatest attention.

The data available on the acidic properties and catalytic activity of borate-containing alumina in alcohol dehydration [22, 23] and olefin isomerization [24, 25] suggest that this material is usable as a catalyst for butene oligomerization. However, almost no information concerning the occurrence of this process on alumina–borate catalysts can be found in the literature.

Here, we report the oligomerization of butenes on borate-containing alumina, including the dependence of the physicochemical properties, activity, and selectivity of the catalyst on its chemical composition; the effect of reaction conditions on the outcomes of oligomerization; and evaluation of the operating stability and regenerability of the catalyst.

EXPERIMENTAL

Borate-containing alumina was prepared from γ-Al_2O_3 (Condea) and orthoboric acid (reagent grade). Alumina pellets, ~3 mm in diameter, were impregnated with a water–methanol solution of orthoboric acid. The impregnated samples were dried at 120°C and were calcined in flowing dry air at 600°C for 2 h. The boron oxide content of the catalysts was varied by varying the orthoboric concentration in the impregnating solution and by performing the impregnation procedure one or two times. The B_2O_3 content of the catalysts was determined from the increase in the sample weight over the weight of the initial alumina support.

The textural properties of the catalysts (specific surface area S_{sp}, pore volume V_{por}, and mean pore diameter D_{mean}) were derived from nitrogen adsorption and desorption isotherms by the BET and BJH methods [26]. The isotherms were obtained using a Micromeritics ASAP 2020 automated analyzer.

The phase composition of the catalysts was studied by X-ray diffraction (DRON-3 diffractometer, β-filtered CuK_α radiation). Diffraction patterns were

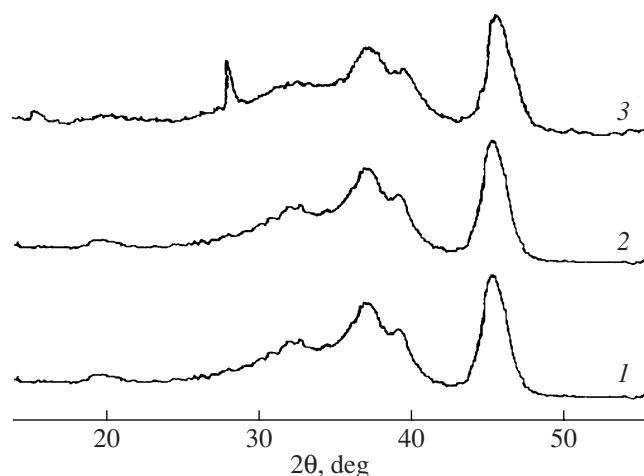**Table 1.** Composition of the butane–butene feedstock used in oligomerization

Component	Content, wt %
Propane	0.6
Propene	0.1
Isobutane	31.7
n-Butane	7.8
Butene-1	15.2
Isobutene	16.9
trans-Butene-2	16.5
cis-Butene-2	10.6
Butadiene-1,3	0.6

Table 2. Textural characteristics of catalyst samples with various B_2O_3 contents

B_2O_3 content, wt %	S_{sp}, m^2/g	V_{por}, cm^3/g	D_{mean}, nm
0.0	196	0.55	10.2
2.6	187	0.53	10.2
4.5	176	0.49	10.2
5.7	170	0.49	10.4
7.7	165	0.49	10.9
8.8	156	0.48	11.3
12.4	136	0.41	11.1

recorded at $2\theta = 10°–60°$ at a scanning speed of 1 deg/min.

The catalysts were characterized by FTIR spectroscopy using a Shimadzu FTIR-8300 spectrometer with a vacuum cell. Catalyst samples were pressed into pellets

Fig. 1. X-ray diffraction patterns from catalysts with B_2O_3 contents of (*1*) 0 (initial γ-Al$_2$O$_3$), (*2*) 4.5, and (*3*) 8.8 wt %.

with a thickness of 15–25 mg/cm^2 and were placed into the spectrometer cell. The cell was pumped at 350°C for 1 h and was then cooled to the ambient temperature. The spectra were recorded in the frequency range from 400 to 6000 cm^{-1} with 4-cm^{-1} resolution, accumulating and averaging the results of 50 measurements.

Butene oligomerization was carried out in a fixed-bed flow reactor (catalyst weight of 4–8 g) at a temperature of $T = 150–200°C$, a pressure of $P = 4.0–8.0$ MPa, and a butene WHSV of $w = 0.5–1.0$ h^{-1}. Before tests, the catalyst samples (particle size of 0.1–0.4 mm) were activated in flowing dry air at 600°C for 0.5 h.

The feed was a commercial butane–butene fraction (catalytic cracking product), whose composition data are presented in Table 1. The oligomerization products were analyzed on-line using two HP 5890 Series II chromatographs with capillary columns and flame ionization detectors. The first chromatograph (60-m-long column, DB-1 phase) was used to determine the composition of the product mixture, including the C$_1$–C$_4$ gases and C$_{5+}$ hydrocarbons, without separating butene-1 from isobutene. The second chromatograph (30-m-long column, K/Al$_2$O$_3$ phase) served to determine the butene-1/isobutene concentration ratio. Chromatograms were recorded and processed using the Multikhrom hardware–software complex.

The total concentration of butenes (*X*) and the conversion of the individual butene isomers were calculated in a standard way from feed and product composition data. The composition of the liquid oligomerization product (C$_{5+}$) was determined by normalizing the peak areas for the C$_{5+}$ components to 100%.

RESULTS AND DISCUSSION

Effect of the Boron Oxide Content on the Properties of the Catalysts

We prepared six catalyst samples containing 2.6 to 12.4 wt % boron oxide (Table 2).

The borate-containing alumina samples, like γ-Al$_2$O$_3$, are mesoporous systems with a unimodal pore-size distribution. However, raising the boron oxide content causes a decrease in S_{sp} and V_{por}. These texture parameters of the initial γ-Al$_2$O$_3$ exceed those of the sample containing 12.4 wt % B$_2$O$_3$ by 60 m^2/g and 0.14 cm^3/g, respectively. The D_{mean} value increases from 10.2 to 11.1 nm on passing from pure alumina to this borate-containing sample. Therefore, modification primarily involves the smallest mesopores of alumina.

According to X-ray diffraction data (Fig. 1), the introduction of up to 4.5 wt % boron oxide into Al$_2$O$_3$ does not alter the phase composition of the latter. The diffraction pattern from the sample containing 8.8 wt % B$_2$O$_3$ shows an extra reflection at $2\theta \approx 28°$, which is assignable to the B$_2$O$_3$ phase (ASTM 13-0570).

According to Sibeijn et al. [27], the interaction of orthoboric acid or boron oxide with γ-Al$_2$O$_3$ above 400°C yields, on the alumina surface, fine-particle alu-
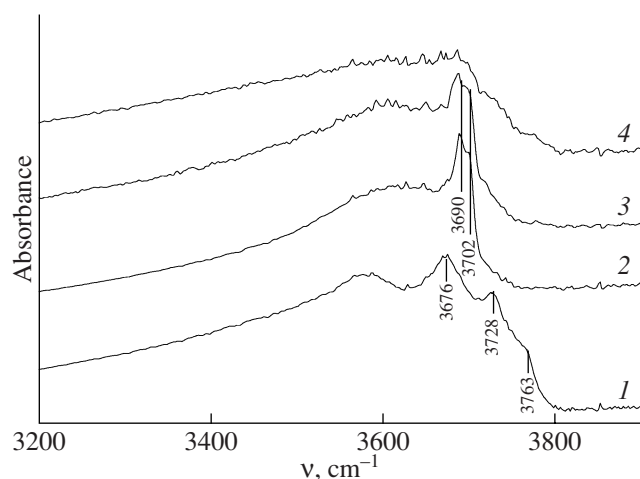
Fig. 2. IR spectra of catalysts with B_2O_3 contents of (*1*) 0 (initial γ-Al_2O_3), (*2*) 2.6, (*3*) 4.5, and (*4*) 8.8 wt %.

Fig. 3. Effect of the B_2O_3 content of the catalyst on (a) the butene conversion and (b) the composition of the oligomerization product at $T = 150$°C, $P = 8.0$ MPa, $w = 1.0$ h^{-1}, and an oligomerization time of 2 h; (a): (*1*) all butenes, (*2*) butene-1, (*3*) isobutene, (*4*) *trans*-butene-2, and (*5*) *cis*-butene-2; (b): (*1*) C_5–C_7, (2) C_8, and (3) C_{9+}.

mina–borate-like structures having Al–O–B–OH fragments and it is these fragments that are responsible for the high acidity and catalytic activity of the modified system as compared to the initial support. It is natural to assume that the extent of this interaction has some limit arising from the fact that, after the introduction of a certain amount of B_2O_3, the alumina surface will be completely covered with alumina–borate structures. At higher modifier contents, part of the boron oxide will be unable to interact with aluminum oxide and will accumulate as a free phase on the catalyst surface. X-ray diffraction data for samples with various B_2O_3 contents indicate that borate-containing aluminum oxide forms in just this way. Therefore, the textural characteristics of the samples containing ≥8.8 wt % boron oxide are likely determined both by the interaction between the initial components and by the presence of free B_2O_3 on the surface.

According to IR spectroscopic data, the state of the surface of the alumina–borate samples differs from the state of the surface of the initial Al_2O_3 and depends on the boron oxide content (Fig. 2). The main evidence of the presence of oxygen-containing boron compounds is the appearance of a strong absorption band in the 1200–1500 cm^{-1} range (not shown in Fig. 2), which is characteristic of B–O stretching vibrations.

Radical changes are also observed in the frequency range 3200–3900 cm^{-1}, which accommodates hydroxyl vibration bands. The surface of the initial γ-Al_2O_3 has three types of hydroxyl groups, which are characterized by absorption bands at 3676, 3728, and 3763 cm^{-1}. These groups are acidic, neutral, and basic, respectively [23]. The modification of alumina with boron oxide (2.6–4.5 wt %) causes the disappearance of these groups and the appearance of B–OH groups giving rise to absorption bands at 3690 and 3702 cm^{-1}, which were reported in earlier publications [23, 25, 27]. According to Bautista et al. [25], the boron atoms in these groups
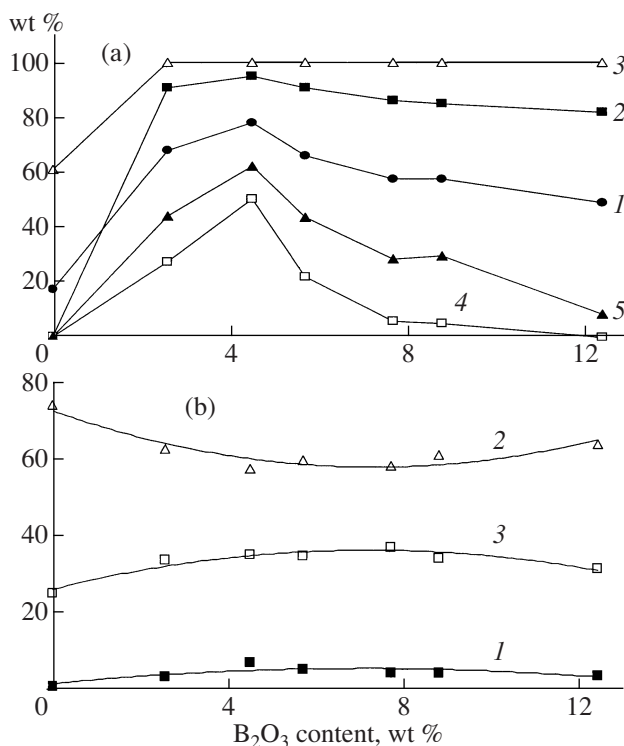
are coordinated to four oxygen atoms. It was demonstrated that this coordination is responsible for the strong Brønsted acidity of the alumina–borate catalysts [24]. Therefore, the B–OH groups that show themselves in the IR spectra of borate-containing alumina indicate the presence of strong Brønsted acid sites on its surface.

The IR spectrum of the sample containing 8.8 wt % boron oxide indicates no B–OH groups. The decrease in the number of these groups or their disappearance caused by the increasing boron oxide content can be explained by the increasing density of the alumina–borate coverage of the alumina surface, which leads to B–OH group condensation yielding B–O–B bonds and to the accumulation of free B_2O_3.

Figure 3 presents the results of butene oligomerization tests for catalysts containing various amounts of B_2O_3. Under the testing conditions, γ-Al_2O_3 shows only a low activity: it catalyzes only the oligomerization of isobutene (~61% conversion). The introduction of the modifier results in a dramatic increase both in the total butene conversion (by a factor of 2.7–4.5) and in the conversions of the individual isomers.

For all of the catalysts examined, the conversions of the individual butenes decreases in the order isobutene > butene-1 > *cis*-butene-2 > *trans*-butene-2,

Table 3. Effects of reaction conditions on the outcomes of oligomerization on the catalyst containing 4.5 wt % B_2O_3

T, °C	P, MPa	w, h^{-1}	X, %	Composition of the C_{5+} fraction, wt %		
				$C_5–C_7$	C_8	C_{9+}
150	4.0	1.0	54.8	5.5	74.3	20.2
200	4.0	1.0	66.3	19.7	62.6	17.7
150	4.0	0.5	89.2	14.8	50.1	35.1
200	4.0	0.5	92.1	29.5	53.9	16.6
150	8.0	1.0	77.8	7.2	57.6	35.2
200	8.0	1.0	82.7	28.8	54.0	17.2
150	8.0	0.5	86.8	10.0	51.4	38.6
200	8.0	0.5	91.3	27.1	48.2	24.7

which is in full agreement with the reported reactivities of these hydrocarbons under acid catalysis conditions [28]. These results enable us to see how the state of the active sites on the surface of the alumina–borate catalysts change as the boron oxide content is raised.

It turned out that the conversion of isobutene, which is the most reactive butene isomer, is independent of the B_2O_3 content of the catalyst and is ~100%. Therefore, at a modifier content of 2.6 to 12.4 wt %, the surface of borate-containing alumina has acid sites sufficiently strong for isobutene oligomerization to take place.

The conversions of *n*-butenes as a function of the boron oxide content of the catalysts pass through a maximum occurring at 4.5 wt % in all cases. At this point, the butene-1 conversion is 94.9%, the *cis*-butene-2 conversion is 50.1%, and the *trans*-butene-2 conversion is 62.0%. The total butene conversion is 77.8%. It follows from these data that the surface of the sample containing 4.5 wt % B_2O_3 has the largest number of strong acid sites capable of oligomerizing not only isobutene and butene-1, but also the butene-2 isomers. Apparently, the number of these sites decreases sharply as the boron oxide content is increased further (>4.5 wt %). For the sample with 12.4 wt % B_2O_3, the *cis*-butene-2 conversion does not exceed 9%, the oligomerization of *trans*-butene-2 is not observed at all, and X takes a lower value of 50%.

These catalytic activity data are in good agreement with the above IR spectroscopic data. Evidently, the B–H groups identified in the IR spectra are indeed strong Brønsted acid sites and the disappearance of these sites at boron oxide contents above 4.5 wt % reduces the activity of the catalyst in the oligomerization of *n*-butenes, particularly the two butene-2 isomers.

As compared to the butene conversion, the group composition of the oligomerization products (C_{5+} hydrocarbons) depends much less strongly on the chemical composition of B_2O_3/Al_2O_3. The proportion of butene dimers (C_8 hydrocarbons) ranges between 57.6 and 64.1 wt %. The amount of C_{9+} hydrocarbons, including molecules containing 9–16 carbon atoms,

varies between 31.8 and 37.3 wt %. However, the 4.5 wt % B_2O_3 catalyst, whose C_{9+} selectivity (35.2 wt % C_{9+} in the C_{5+} fraction) is comparable with that of the other catalysts, shows the highest cracking power (7.2 wt % $C_5–C_7$ in the C_{5+} fraction). This may be another manifestation of the increased strength of the acid sites on the surface of this catalyst [28].

Effect of Reaction Conditions on the Outcomes of Oligomerization

Butene oligomerization on various anion-modified metal oxides, including borate-containing alumina, generally occurs at $T = 140–200$°C and $P = 4.0–8.0$ MPa. These conditions ensure high activity and operating stability of the catalysts owing to the near-critical state of the reaction medium and in situ extractive regeneration taking place [17, 20, 21]. Butene oligomerization data obtained for the 4.5 wt % B_2O_3 catalyst using a two-level experimental design [29] are presented in Table 3.

As the oligomerization temperature is raised from 150 to 200°C ($w = 1.0$ h^{-1}, $P = 4.0$ MPa), X increases by 11.5% and the $C_5–C_7$ content of the C_{5+} fraction increases from 5.5 to 19.7 wt % because of the intensification of oligomer cracking. Reducing the butene WHSV from 1.0 to 0.5 h^{-1} exerts a similar effect on oligomerization. The strongest effect from the decrease in w is observed at $P = 4.0$ MPa: X increased from 54.8 to 89.2% at 150°C and from 66.3 to 92.1% at 200°C.

The favorable effect of increasing pressure is most pronounced at $w = 1.0$ h^{-1}. As the oligomerization pressure is raised from 4.0 to 8.0 MPa, the total butene conversion increases by 23.0 and 16.4% at 150 and 200°C, respectively. The reduction of w to 0.5 h^{-1} weakens the pressure effect: X at pressures of 4.0 and 8.0 MPa takes similar values of 87–89% at 150°C and 91–92% at 200°C, respectively. Note that an increase in pressure in this case suppresses the cracking reactions because they are accompanied by an increase in the number of moles. It is likely because of this that the $C_5–C_7$ content

of the oligomerization product at $P = 8.0$ MPa is 2.4–4.8 wt % lower than the same parameter at $P = 4.0$ MPa.

The best combination of catalytic activity and selectivity is observed at $T = 150°C$, $P = 8.0$ MPa, and $w = 0.5$–1.0 h^{-1}. Under these conditions, the alumina–borate catalyst containing 4.5 wt % B_2O_3 affords a total butene conversion of 77.8–86.8% and the total concentration of butene oligomers in the liquid product is at least 90 wt %. About 50 wt % of these oligomers are C_8 hydrocarbons. Similar results were obtained for the oligomerization of the butane–butene fraction on tungstate-containing titania [17].

Effects of the Catalyst On-Stream Time and Regeneration on the Outcomes of Oligomerization

The operating stability of the 4.5 wt % B_2O_3 catalyst is illustrated by the plots shown in Fig. 4. Over an on-stream time of 14 h, the isobutene conversion is 100% and the butene-1 conversion remains at the 91.6% level. By contrast, the conversion of the butene-2 isomers changes greatly over the above on-stream time: the *cis*-butene-2 conversion decreases by a factor of 2.5; the *trans*-butene-2 conversion, by a factor of 1.5. However, the decrease in the total butene conversion does not exceed 13% from the initial level of 77.8%. The observed deactivation of the catalyst can obviously be due to the gradual poisoning of the strongest active sites on its surface by oligomerization products.

In the course of oligomerization, the amount of C_{9+} hydrocarbons decreases from 35.2 to 26.4 wt % and the amount of C_5–C_7 components decreases from 7.2 to 3.5 wt % (Table 4). This is further evidence that the
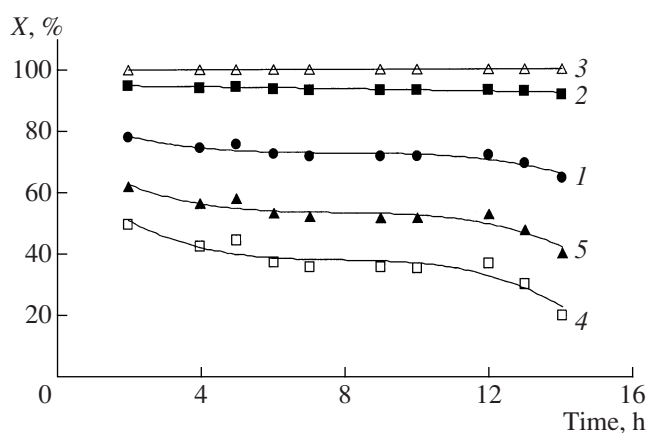

Fig. 4. Butene conversion versus time on stream for the 4.5 wt % B_2O_3 catalyst at $T = 150°C$, $P = 8.0$ MPa, and $w = 1.0$ h^{-1}: (*1*) all butenes, (*2*) butene-1, (*3*) isobutene, (*4*) *trans*-butene-2, and (*5*) *cis*-butene-2.

number of strong acid sites on the catalyst surface decreases as the catalyst is operated for a long time.

The catalyst deactivated by 14-h-long operation was treated with dry air at 600°C for 2 h without being taken out of the reactor. Tests of the regenerated catalyst demonstrated that it had completely restored its initial activity and selectivity (Table 4). Therefore, the deactivation of borate-containing alumina is reversible and apparently causes no chemical changes in its active component. No chemical changes in the catalyst are also observed upon the high-temperature burnout of the hydrocarbons adsorbed on the catalyst surface during oligomerization.

Table 4. Effects of the time on stream on the total butene conversion and on the composition of the liquid oligomerization product (C_{5+}) for the catalyst containing 4.5 wt % B_2O_3*

Time, h	A				B			
	X, %	composition of the C_{5+} fraction, wt %			X, %	composition of the C_{5+} fraction, wt %		
		C_5–C_7	C_8	C_{9+}		C_5–C_7	C_8	C_{9+}
2	77.8	7.2	57.6	35.2	75.8	6.3	56.2	37.5
3	–	–	–	–	75.0	7.6	59.2	33.2
4	74.6	6.2	63.4	30.4	74.8	7.3	61.4	31.3
5	75.5	5.6	64.1	30.3	73.6	7.2	62.5	30.3
6	72.5	5.6	63.8	30.6	73.2	6.4	60.8	32.8
7	71.8	5.3	68.6	26.1	–	–	–	–
9	71.7	5.1	69.0	25.9	–	–	–	–
10	71.6	8.7	64.6	26.7	–	–	–	–
12	72.2	3.6	63.8	32.6	–	–	–	–
13	69.3	3.6	67.9	28.5	–	–	–	–
14	64.9	3.5	70.1	26.4	–	–	–	–

Note: A is the original sample, and B is the regenerated sample.
 * Oligomerization conditions: $T = 150°C$, $P = 8.0$ MPa, and $w = 1.0$ h^{-1}.

Thus, borate-containing alumina is usable as an active and selective butene oligomerization catalyst. By varying the boron oxide content, it is possible to control the activity of the catalyst in the conversion of particular butene isomers. The deactivation of the alumina–borate catalyst during oligomerization is reversible, and the properties of the catalyst can be restored completely by oxidative regeneration.

The commercialization prospects for borate-containing alumina as an oligomerization catalyst are due not only to its catalytic properties (which are similar to those of the catalysts based on sulfate- and tungstate-containing titania), but, to a greater extent, to the availability of the raw materials for its production and to the vast experience in the manufacturing of alumina catalysts.

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