<center>

DOMESTIC
CATALYSTS

</center>

Experience in the Development and Introduction of Aluminochromic for Fluidized-Bed Isobutane Dehydrogenation

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Abstract—A summary of experience in the development of a microspherical aluminum−chromium catalyst isobutane dehydrogenation to isobutylene using the Yarsintez technology is presented. The development dynamics of KDI industrial catalysts based on a new boehmite support is considered. The relationships between elemental and phase compositions of catalysts and their operational characteristics are found. A boehmite support was obtained according to a new two-stage scheme, including the hydrothermal treatment of a thermal decomposition product of gibbsite agglomerates with a required size. This technology makes it possible to control the phase composition of a support and the physicomechanical properties of catalysts and their catalytic properties, which made it possible to obtain KDI, KDI-M, and KDI-M1 catalysts. The most important stages of their introduction into commercial operation at Nizhnekamskneftekhim are described. The KDI-M industrial catalyst provides a stable yield of isobutylene of 33−37% during the isobutane dehydrogenation and a yield of methylbutenes of 30% during the isopentane dehydrogenation. The catalyst consumption is 2−3 kg per ton of isobutylene produced. The ways are proposed for the improvement of a catalyst and the optimization of reactor equipment on the basis of monitoring the catalyst operation results. The KDI-M1 industrial catalyst modified with a silicon-containing inorganic complex is better than earlier products of this series in its activity and selectivity according to laboratory tests and is ready for production.

Keywords: dehydrogenation, microspherical catalysts, isobutylene, introduction

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INTRODUCTION

Nonoxidative isobutane dehydrogenation in the presence of aluminum chromium catalysts is used for the synthesis of corresponding olefins to produce synthetic rubbers, fibers, films, and plastics from them [1−3]. The technology developed at Yarsintez (foreign name, FBD-4) is designed for the fluidized-bed synthesis of olefins at atmospheric pressure on a microspherical catalyst with grain sizes of 20−150 μm circulating in a reactor−regenerator system [4, 5]. The heat required for the endothermic dehydrogenation process is supplied to the reaction zone by a hot regenerated catalyst that undergoes alternating cycles of high-temperature redox dehydrogenation and regeneration during operation.

The most common large-capacity product in the production of catalysts for domestic petrochemistry is microspherical isobutane dehydrogenation catalysts. They are produced in quantities of ~12000 t/year and are loaded into industrial plants in amounts of ~250−600 t.

Alumina−chromium catalysts are obtained using two basic technologies: the spraying−drying of a catalyst suspension and the impregnation of alumina [6−10]. The first technique is used to obtain IM-2201 cat-

alyst [8, 9] and was developed by Yarsintez (Yaroslavl, Russia) in the 1970s [10]. It is industrially produced at the Kauchuk (Sterlitamak, Russia) plant and Novokuibyshev Petrochemical Company (Novokuibyshevsk, Russia). A main disadvantage of this catalyst is large particles of more than 125 μm in size, which are forbed by the adhesion of smaller ones. Primary alumina and kaolin particles are bound by fragile coagulation contacts during synthesis. Such grains are rapidly destroyed under hard industrial conditions. The resulting particles (<10 μm), which consist mainly of kaolin and chromium oxide [11], are carried away from the reactor block [8] and settle in waste heat boilers to reduce the free cross section and efficiency of heat exchange. This raises the pressure in the system and lowers the performance of the dehydrogenation unit. Larger particles continue to circulate in the system to form an equilibrium catalyst in which the amount of fractions smaller than 71 μm is 70 wt % [8]. Constant additional loading into the reactor is required during the operation of this catalyst because of its low abrasion resistance. This results in its high consumption, up to 25 kg per ton of olefin [8].

AOK, KDM, and KDI catalysts are produced via the impregnation of alumina supports, which have the

highest strength of grains and the lowest consumption per ton of olefin produced. AOK-73-21 [12], AOK-73-24 [13], and AOK-73-24 (RF) [14] dehydrogenation catalysts are produced from a product of the thermochemical activation of aluminum trihydroxide, which has higher mechanical strength and activity than IM-2201 [15]. AOK catalysts are currently produced at Katalizator (Novosibirsk, Russia) [14]. AOK-73-24 (RF) catalyst is exported to Saudi Arabia.

Until 2008, AOK-73-21 was used in mixtures with IM-2201 at Nizhnekamskneftekhim. In 2006, 50 tons of experimental MKD catalyst was mixed with IM-2201 and tested at the Shchelkovo Catalyst Plant (Shchelkovo, Russia). AOK-73-21 and MKD catalysts were not purchased due to the instability of their phase and chemical compositions and high abrasive activity, even though the mixtures of such catalytic systems improve the profitability of production by reducing the catalyst consumption and the expenditures on the purchase of fresh batches.

The KDM catalyst was developed by the Boreskov Institute of Catalysis (Novosibirsk, Russia) in partnership with Sintez (Barnaul, Russia). The catalyst production technology is based on an $Al_2O_{3-x}(OH)_2 \cdot nH_2O$ ($x = 0-0.28$; $n = 0.03-1.8$) amorphous nanostructured hydroxide-oxide compound as a support synthesized via the centrifugal thermal shock activation of trihydroxide aluminum on a TSEFLAR centrifugal flash reactor [15–20]. As a result, higher activity and selectivity were achieved as compared to to catalysts based on those supports and obtained via the thermochemical activation of aluminum trihydroxide [15]. KDM is operated in mixtures with IM-2201 catalyst in approximately equal proportions.

The Laboratory of Adsorption and Catalytic Processes of the Kazan Federal University in partnership with Nizhnekamskneftekhim developed KDI microspherical aluminochromium catalysts to solve the problem of reducing catalyst consumption.
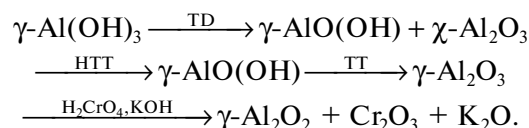
In this paper, we consider the dynamics of developing KDI, KDI-M, and KDI-M1 industrial catalysts based on a new boehmite support obtained via hydrothermal treatment of a product of the thermal decomposition of gibbsite agglomerates with a required size. The relationships between elemental and phase compositions of catalysts and their performance characteristics are given, along with results from implementation at Nizhnekamskneftekhim.

CREATION, INTRODUCTION, AND OPERATION OF KDI CATALYSTS

The first pilot series of KDI catalyst was produced at the Ishimbai Specialized Catalyst Plant in the amount of 300 tons on an SA-1001 support (Engelhard, United States). The product was recommended for use in isobutane dehydrogenation units instead IM-2201 catalyst according to results from pilot tests

at the Nizhnekamskneftekhim plant, but a disadvantage was high cost of the imported support.

Available gibbsite was therefore used for the second version of KDI catalyst as a precursor of a microspherical alumina support, as iron, silicon, and sodium impurities in its composition have no appreciable effect on the performance of fluidized bed catalysts. A sequential two-stage scheme, according to which a product of thermal decomposition of gibbsite agglomerates of the required size and an aluminum-chromium catalyst based on it undergo the hydrothermal treatment, was developed to obtain a boehmite support [21]:

$$\gamma\text{-Al(OH)}_3 \xrightarrow{\text{TD}} \gamma\text{-AlO(OH)} + \chi\text{-Al}_2\text{O}_3$$
$$\xrightarrow{\text{HTT}} \gamma\text{-AlO(OH)} \xrightarrow{\text{TT}} \gamma\text{-Al}_2\text{O}_3$$
$$\xrightarrow{\text{H}_2\text{CrO}_4,\text{KOH}} \gamma\text{-Al}_2\text{O}_2 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}.$$

The thermal decomposition (TD) of GD 00 gibbsite (Gb) agglomerates containing SiO_2. Na_2O, and Fe_2O_3 impurities in amounts of 0.01, 0.03, and 0.02 wt %, respectively, was performed in the air under atmospheric pressure. As a result, mixed aluminum hydroxide and oxide compounds that include residual gibbsite (χ-Al_2O_3) form, depending on temperature: coarse-crystalline (Bm) and fine-crystalline (FBm) boehmites, form along with γ-Al_2O_3 during the decomposition of Bm and FBm. The agglomerates retain their shape due to pseudomorphism, but had low strength and thermal stability. The abrasion resistance of grains (RA) falls from 92 to 72%, preventing their use as microspherical supports. Subsequent hydrothermal treatment (HTT) [22, 23] gives a single-phase or heterophase microspherical support with strong crystalline contacts between primary particles and abrasion resistance as high as 90–98%. Such treatment allows us to control the phase composition of aluminum hydroxides and oxides, the sizes of crystals, the parameters of the porous system, and the acidic properties of the surface (Fig. 1). This technology makes it possible to control the properties of microspherical supports and obtain boehmite agglomerates from single phases with RAs up to 88–98% to polyphase boehmite-$\chi(\gamma)$-Al_2O_3 with lower abrasion resistance (RA = 80–90%). New KDI catalysts were synthesized from such supports for isobutane dehydrogenation, where the optimum Cr_2O_3:K_2O ratio was found to be 9.3–10.5 [24]. Table 1 contains the properties of KDI laboratory catalysts with different content of chromium and potassium oxides. High yields of isobutylene and low yields of cracking products (C_1–C_3 hydrocarbons) are observed for the K-3, K-4, and K-5 samples with Cr_2O_3 concentrations of 9.5–12.5 wt %. The high activities of these samples (PY = 49–51%) is due to the formation of X-ray amorphous Cr_2O_3 clusters on the catalyst's surface, as evidenced by an increased intensity of the signal at 552–564 cm^{-1} in the Raman spectra from the vibrations of a Cr(III)$_{oct}$–O bond (Fig. 2a). The higher selectivity to 93% to
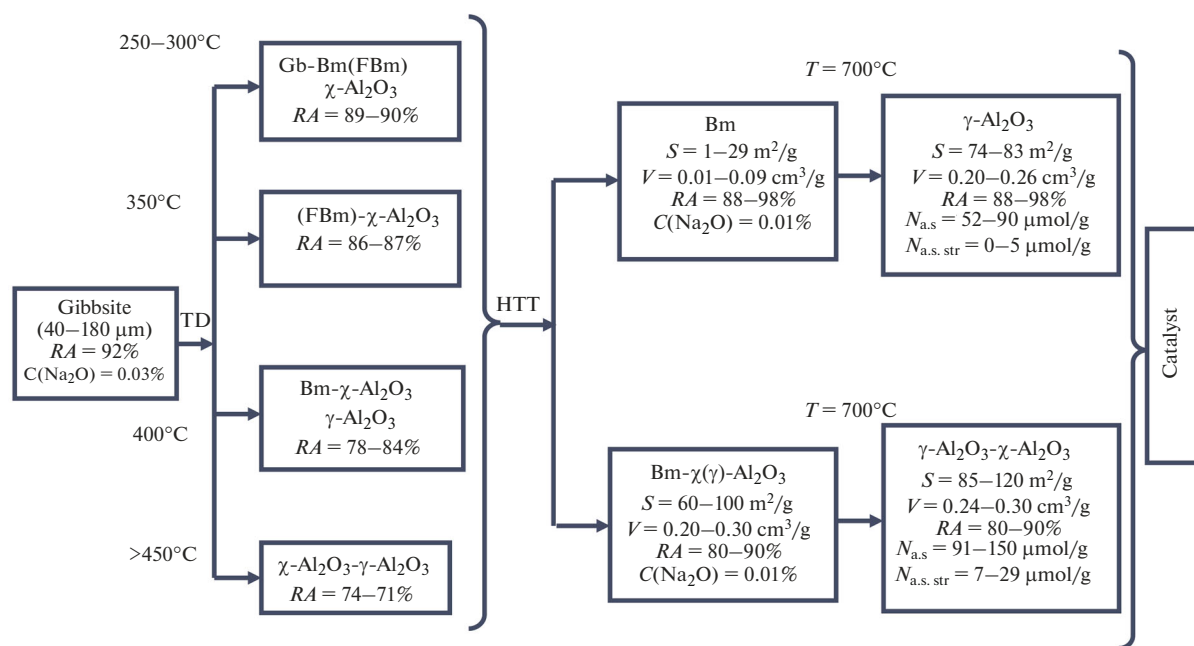
Fig. 1. Scheme for controlling the properties of boehmite and alumina microspherical supports during the thermal decomposition of gibbsite agglomerates and hydrothermal treatment of products (S is the specific surface area (Brunauer−Emmett−Teller model), V is the volume of pores, $N_{a.s}$ is the total concentration of acid sites (temperature-programmed desorption of ammonia), and $N_{a.s.str}$ is the concentration of strong acid sites with energies of ammonia desorption of more than 150 kJ/mol, temperature-programmed desorption of ammonia).

isobutylene is due to an increase in interaction between Cr(III) ions: the intensity of the β-signal in EPR spectra grows, indicating a drop in the number of the strongest coordinatively unsaturated sites (Fig. 2b). Table 1 shows that the proportion of acid sites with ammonia desorption energies of more than 150 kJ/mol falls from 12.7 to 8.4 μmol NH_3/g upon raising the concentration of Cr_2O_3 from 9.5 to 12.5 wt %. This slows the rate of formation of hydrocarbon deposits with no increase in the rates of cracking and isobutane conversion.

The abrasive activity of the single-phase boehmite support is comparable to that of the initial gibbsite [21]. It is 3.5 times lower than that of products of the thermochemical activation (TCA) of gibbsite and catalysts based on them, due to the low density of protrusions above the surface of grains and high strength of crystallization contacts between primary particles in the agglomerates (Table 2).

A technological line for producing the second KDI catalyst based on a new boehmite with a capacity of 1000 tons per year has been designed at the Karpov Chemical Plant (Mendeleevsk, Russia). Pilot tests of the catalyst in batches of 25 to 290 tons were performed in the reactor blocks of units DB-2 and BK-2 of the isobutane dehydrogenation plants at Nizhnekamskneftekhim [25]. 2201 catalyst was loaded into parallel blocks. When the KDI catalyst (second version) was loaded, there was a drop in the temperature difference between the upper and lower parts of the reactor, an improvement in transportation of equilibrium catalyst along the reactor-regenerator circuit, a 1.5−2.0% increase in the yield of isobutylene, a 0.5−0.8% drop in the yield of cracking products, and a 5.4% increase in selectivity toward isobutylene. The consumption of a mixture of operating catalysts per ton of isobutylene produced fell from 30 to 6−11 kg.

The catalyst was modified with SiO_2, which does not contain Lewis acid sites, in amounts of 2.5−4.5 wt % to improve performance indicators. More polymerized chromates formed on the SiO_2 surface, and Cr_2O_3 clusters formed at smaller amounts of chromium than with γ-Al_2O_3 [26]. We found that SiO_2 is distributed in the catalyst over the surface as silicon oxide fragments and raises its total acidity, due to the formation of additional acid sites of weak and moderate strength with a reduced number of strong sites [27] (Tables 3 and 4). The amount of Cr(III) compounds grows, due to a drop in the concentration of the Cr(VI) compounds. There was increased polymerization of chromates, due to lower stabilization by the support and a drop in the number of bonds between aluminum, silicon, and chromates on the catalyst's surface [27]. This allowed us to obtain a more active and selective sample than the KDI catalyst (Table 4).

Table 1. Properties of KDI catalyst samples (second version) in the isobutane dehydrogenation reaction in a fluidized catalyst bed (temperature of dehydrogenation, 570°C; tests were performed in accordance with TU 2173-075-00206457-2007)

Parameters	Parameters for samples				
	K-1	K-2	K-3	K-4	K-5
$C(Cr_2O_3)$, wt %	6.6	9.0	9.5	11.5	12.5
$C(K_2O)$, wt %	0.7	0.9	1.0	1.1	1.3
$C[Cr(VI)]$, wt %	2.1	2.2	2.5	2.5	2.7
S_{BET}, m²/g	79	80	77	67	73
V, cm³/g	0.23	0.23	0.22	0.22	0.21
$\Sigma N_{a.s}$, µmol NH₃/g	80.0	77.5	72.4	69.0	68.3
$N_{a.s.}$ (E_d > 150 kJ/mol), µmol NH₃/g	12.7	10.2	9.7	9.1	8.4
Rate of iso-C_4H_{10} conversion, µmol/(g_{cat} s)	1.81	2.21	2.30	2.34	2.38
Rate of C_1-C_3 hydrocarbon formation, µmol/(g_{cat} s)	0.33	0.38	0.42	0.38	0.34
Selectivity by iso-C_4H_8%	92	92	92	92	93
PY, %	39	47	49	50	51
DY, %	87	87	87	89	87

S_{BET} is the specific surface area (Brunauer−Emmett−Teller model), V the volume of pores, $N_{a.s}$ the concentration of acid sites (temperature-programmed desorption of ammonia), E_d the energy of ammonia desorption, PY is the yield of isobutylene per passed isobutene, and DY is the yield of isobutylene to decomposed isobutane.

The industrial production of KDI-M modified catalyst with a capacity of 2000 t/year was organized at the Nizhnekamskneftekhim for its own needs in 2014 [28], and another production line with a capacity of 3000 t/year was put into operation in 2019. When the KDI-M catalyst was loaded into BK-2 and DB-2 units, the yield of isobutylene relative to the KDI catalyst rose by 3−4%, the yield of cracking products fell
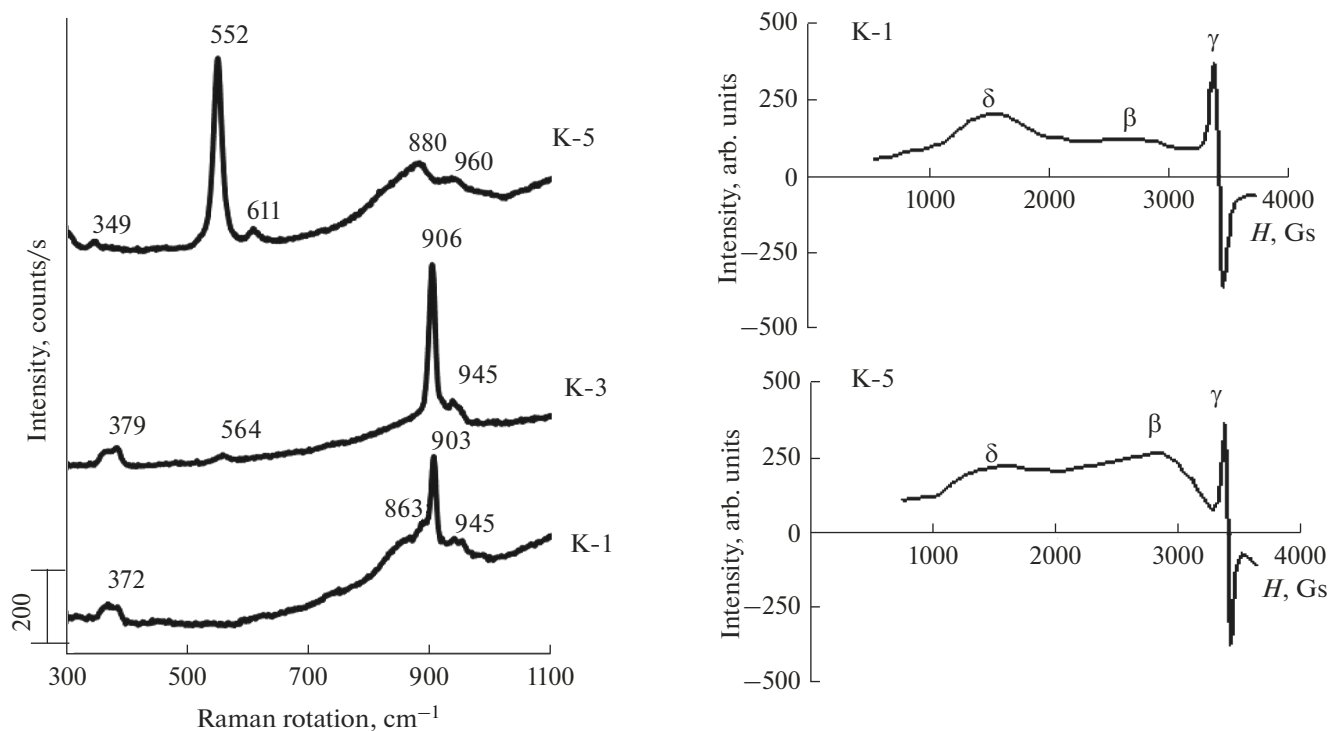

Fig. 2. Spectra of KDI catalyst samples (second version): (a) Raman spectra and (b) EPR spectra (−196°C).

Table 2. Abrasive activity and physicomechanical properties of microspherical supports

Sample	Properties				
	A, g/(m^2 h)	RA, %	HV, N/mm^2	$C \times 10^3$, μm^{-2}	Φ
Gibbsite (40−200 μm)	0.120	65	348	0.27	0.81
Boehmite support obtained via subsequent thermal and hydrothermal treatments of gibbsite (40−200 μm)	0.121	88	613	0.15	0.85
TCA of gibbsite (70−315 μm)	0.413	89	772	1.65	0.78
TCA of gibbsite combined with mechano-chemical activation (70−315 μm)	0.426	90	824	1.80	0.76

A is abrasive activity, C the number of protrusions above the surface of a grain reduced to unit surface, HV is the Vickers microhardness of grains, and Φ the coefficient of a grain's sphericity (the ratio of the smallest to the largest grain size is the average value of fifty measurements).

Table 3. Properties of initial KDI catalyst (sample K-3) and its modified SiO$_2$ samples

C(SiO$_2$), wt %	S_{BET}, m^2/g	V, cm^3/g	C[Cr(VI)], wt %	$\Sigma N_{a.s}$, μmol NH$_3$/g	$N_{a.s}$, μmol NH$_3$/g		
					$E_{des} < 100$ kJ/mol	100 kJ/mol $< E_{des}$ < 150 kJ/mol	$E_{des} > 150$ kJ/mol
0	77	0.22	2.5	72.4	9.3	9.3	9.3
2.5	73	0.22	1.9	93.7	12.9	78.0	2.8
4.5	74	0.22	1.6	102.8	15.7	85.5	1.6
7.5	70	0.22	1.4	109.6	13.8	95.6	0.2

S_{BET} is the specific surface area (Brunauer−Emmett−Teller model), V is the volume of pores, $N_{a.s}$ is the concentration of acid sites (temperature-programmed desorption of ammonia), and E_d is the energy of ammonia desorption.

by ~1%, and the overhaul run of the reactors went from 270 to 400 days. The current performance indicators for KDI-M catalyst remain at the same level.

Around 180 tons of KDI-M catalyst was also loaded gradually into block no. 1 of the I-2 unit for isopentane dehydrogenation until the IM-2201 catalyst circulating in it was displaced. During tests, the average yield of methylbutenes in block no. 1 where KDI-M catalyst was loaded was 2% higher than in block no. 2 with IM-2201 catalyst. It was 30.4% in August 2017 and 29.5% in September (Fig. 3). The selectivity toward methylbutenes was 72−73% at a catalyst consumption of 4−8 kg per ton of olefins produced. At the same time, the catalyst consumption was more than 20 kg/t of olefins in block no. 2 [21].

The consumption of KDI-M catalyst was 2−3 kg per ton of isobutylene on new IF-1 and IF-2 isobutane dehydrogenation units under conditions of operating exclusively with this catalyst, and the loaded catalyst samples' period of residence in the dehydrogenation units grew considerably.

Results from monitoring the operation of these units showed that the activity and selectivity of all industrial catalysts gradually fell during such long periods of operation because of irreversible deactivation associated with changes in the state of the active component (Fig. 4). This requires a higher temperature of dehydrogenation but does not allow a return to the catalytic performance of a fresh catalyst. An equilibrium catalyst is therefore periodically replaced with a fresh one in amounts of 25−30 tons, even at low consumption of the catalyst per ton of olefin produced, to equalize the effect of irreversible deactivation and

Table 4. Catalytic parameters of SiO$_2$ modified KDI catalyst samples during isobutane dehydrogenation in a fluidized bed (temperature of dehydrogenation, 570°C; tests were performed in accordance with TU 2173-075-00206457-2007)*

Parameters	Values at C(SiO$_2$), wt %			
	0	2.5	4.5	7.5
Conversion rate of iso-C$_4$H$_{10}$. μmol/(g$_{cat}$ s)	2.30	2.28	2.37	2.22
Formation rate of C$_1$−C$_3$ hydrocarbons, μmol/(g$_{cat}$ s)	0.42	0.32	0.34	0.28
Selectivity by iso-C$_4$H$_8$, %	91.9	93.6	93.1	94.3
PY, %	49.4	49.6	51.5	48.5
DY, %	86.7	89.8	88.9	89.5

* PY is the yield of isobutylene per passed isobutene; DY is the yield of isobutylene to decomposed isobutane.
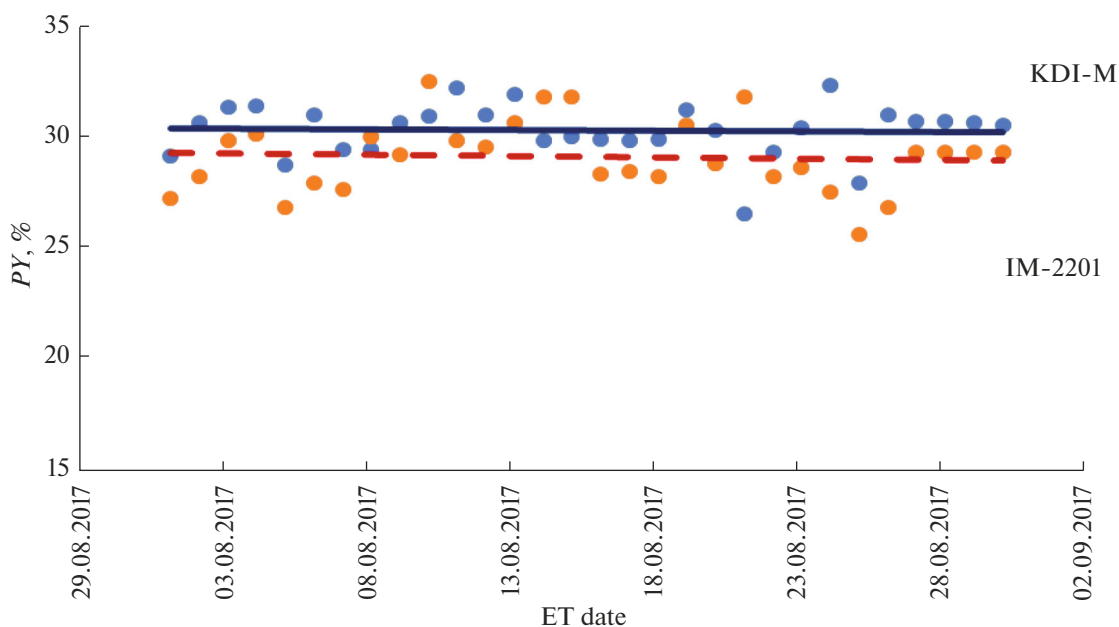
Fig. 3. Yield of C_5H_{10} hydrocarbons per passed hydrocarbons catalysts in *iso*pentane dehydrogenation units of the I-2 installation.

minimize the drop in olefin production under industrial conditions.

It is known [29−34] that irreversible deactivation is due to a combination of three factors: the agglomeration of particles of Cr(III) and Cr(VI) oxygen compounds, the gradual incorporation of Cr(III) ions into the support's structure to form aluminochromium spinel, and the formation of α-Cr_2O_3. We studied the change in the properties of aluminum-chromium catalysts under prolonged laboratory reactor conditions at at reaction and regeneration temperatures corresponding to the industrial dehydrogenation of isobutane to isobutylene. It was found for the first time [35] that α-Cr_2O_3 crystals formed on supports with low specific surface areas ($\sim$60 m^2/g) stabilize the highly active phases of amorphous Cr_2O_3 and polychromates to prevent the agglomeration of their particles during repeated redox cycles. This is due to the formation of $Cr_{cryst}^{3+}-O-Cr_{am}^{3+}$ and $Cr_{cryst}^{3+}-O-Cr^{6+}$ interfacial bonds in the resulting two-phase (α-Cr_2O_3-am-Cr_2O_3 and

α-Cr_2O_3-polychromate) or three-phase (polychromate-α-Cr_2O_3-am-Cr_2O_3) fragments, which stabilizes the catalytic performance properties during long-term operation.

While improving the catalyst, we understood the efficiency of its operation was also defined by the hydrodynamics of the process [36]. The internal components of dehydrogenation units and the fractional composition of the catalyst must be adapted to each other. Current dehydrogenation units were designed for the IM-2201 catalyst with different destruction kinetics and average sizes of microspherical grains. We therefore developed mathematical models for the reactors of the BK-2 and DB-2 units, from which we proposed a list of measures for their modernization that are currently being implemented. This created the basis for developing the KDI-M1 catalyst modified with a silicon-containing inorganic complex compound. Tests of the industrial sample versus other industrial analogs confirmed its high efficiency (Table 5).

Table 5. Catalytic parameters of isobutane dehydrogenation in a fluidized catalyst bed (temperature of dehydrogenation, 570°C; tests were performed in accordance with TU 2173-075-00206457-2007)

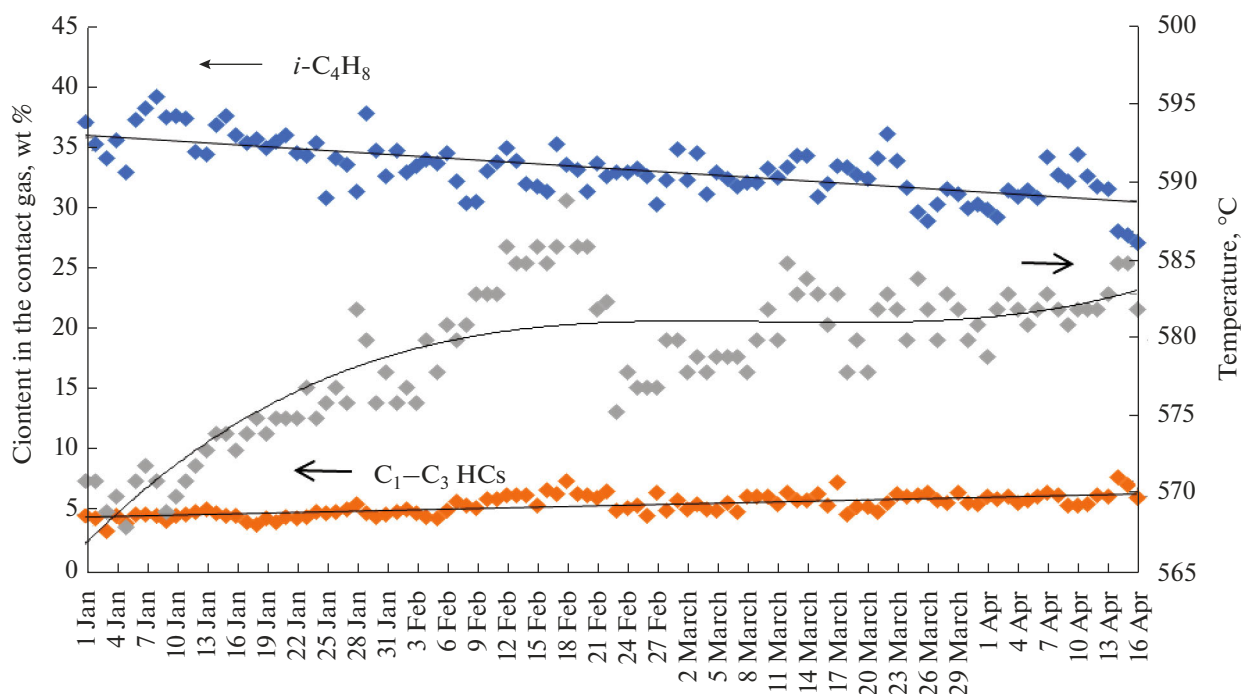| Indicators	KDI-M1	KDI-M	KDI (second version)
PY, %	51	49	45
DY, %	91	88	87
RA, %	90	92	85
A, g/(m^2 h)	0.18	0.18	0.25
Year	2018	2012	2007

Fig. 4. Results from monitoring the operation of the isobutane dehydrogenation reactor.

CONCLUSIONS

It has been shown that our two-stage scheme for the synthesis of a boehmite support via the hydrothermal treatment of a product from the thermal decomposition of gibbsite agglomerates allows us to control the phase composition, physicomechanical properties, and catalytic properties of catalysts. Technologies for the production of microspherical alumina–chromium catalysts of the dehydrogenation of isobutane, created according to the two-stage scheme, were put into commercial operation at the Nizhnekamskneftekhim.

The KDI-M industrial catalyst ensures a stable isobutylene yield of 33−37% in isobutane dehydrogenation, while the yield of methylbutenes in isopentane dehydrogenation is 30%. The catalyst consumption fell from 25 to 2−3 kg per ton of isobutylene produced. There was an increase in the profitability of isobutylene production at a cost comparable to that of domestic analogues obtained by spraying–drying technologies and alumina support impregnation due to reduced consumption of the catalyst and a drop in the cost of fresh batches.

Modification with a silicon-containing inorganic complex resulted in the development of the KDI-M1 catalyst, which are supreior to the KDI and KDI-M catalysts in performance according to test results under laboratory conditions and is ready for industrial application.

Ways of improving the catalyst are the stabilization of its highly active phases of amorphous Cr_2O_3 and polychromates via the formation of a crystalline α-Cr_2O_3 phase on the surface, and optimizing its hydrodynamic properties.

CONFLICT OF INTEREST

The authors declare they have no conflicts of interest.

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