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Pilot Tests of the Microspherical Aluminochromium KDI-M Catalyst for *iso*-Butane Dehydrogenation

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Abstract—Results from pilot tests of microspherical aluminochromium KDI-M catalyst mixed with IM-2201 in a large-scale unit (Nizhnekamskneftekhim) for *iso*-butane dehydrogenation are discussed. Compared to KDI catalyst, its modified analogue KDI-M is more active and selective; the optimized grain-size composition and mechanical strength ensures higher yields of *iso*-butylene and longer nonstop operation (up to 400 days) of the reactor unit.

Keywords: aluminochromium catalyst, fluidized bed, dehydrogenation, *iso*-butylene, runlife

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INTRODUCTION

The dehydrogenation of lower paraffins in a fluidized bed of microspherical aluminochromium catalyst is the main way of producing the C₄–C₅ olefins used in the production of polymer materials (plastics, synthetic rubbers, and fibers), high-octane additives to fuels, solvents, and other products of organic synthesis.

The operational and economic indicators of the dehydrogenation of lower paraffins in a fluidized bed depend not only on the characteristics of the catalyst (its activity and selectivity) and the thermodynamic conditions (temperature and pressure) but on the hydrodynamics of the fluidized bed of the reactor unit as well. The latter is in turn determined by the combined effect of the parameters of the technological process and the structural–mechanical properties and grain-size composition of the catalyst.

The main catalyst for the dehydrogenation of lower paraffins in a fluidized bed is IM-2201 [1], developed in the 1960s and produced by spray drying suspensions of aluminum hydroxide, kaolin clay, chromic acid, potassium hydroxide, and potassium liquid glass [2–4]. The features of this technology are such that coagulation-type contacts form between the aggregates that make up a micrograin of IM-2201, and these contacts determine the low mechanical strength of the catalyst [5]. This in turn results in high consumption of the

catalyst per unit of produced olefin, and in substantial environmental pollution by dust containing hexavalent chromium. Microspherical aluminochromium catalysts, obtained by impregnating a premade alumina support with solutions of an active component, a promotor, and a modifying agent, are therefore more promising. Impregnation-type systems include the catalysts AOK-73-21(24) [4], KDM [7], SPS [8, 9], IM-2201 P [10], and KDI [11, 12], along with its modified analogue KDI-M [13]. A fundamental difference between these catalysts is the technology for producing their supports. For example, AOK-73-24 and KDM catalysts are produced using products of the thermochemical activation (TCA) [14, 15] and centrifugal thermal activation (CTA) of gibbsite [7, 16], respectively. These catalysts have higher activities than MI-2201 [7, 10, 17] and have long been used in industry, contributing to a considerable reduction in the rate of catalyst consumption [7].

KDI catalyst and its advanced analogue KDI-M use a support obtained by the sequential thermo-hydrothermal treatment of gibbsite [11, 12].

The use of the KDI catalyst mixed with IM-2201 in industrial plants for *iso*-butane dehydrogenation was described in [18, 19]. This work continues our studies on the modification and commercial application of KDI catalyst. Below, we present the results from pilot

Operating indicators of microspherical aluminochromium catalysts

Indicator	Catalyst		
	IM-2201	KDI	KDI-M
Activity, %*	46	47	48
Selectivity, %*	86	85	90
Resistance to wear M_n , %	65	89	86

*Under laboratory conditions during the dehydrogenation of *iso*-butane at 570°C.

tests of its advanced analogue, modified KDI-M catalyst, loaded in a reactor unit for *iso*-butane dehydrogenation (Nizhnekamskneftekhim) in mixtures with IM-2201.

EXPERIMENTAL

Our objects of study were industrial microspherical aluminochromium catalysts, such as:

- mixture-type IM-2201; and
- impregnation-type domestic KDI (TU (Technical Specifications) 2173-075-00206457–2007) and KDI-M (TU 217341-001-02066730–2014).

Under laboratory conditions, their catalytic properties were determined for *iso*-butane dehydrogenation in the fluidized bed of catalyst in a steel tubular reactor. The volume of the loaded sample was 100 cm³, the reaction temperature was 570°C, and the regeneration temperature was 650°C. To keep the temperature in the reactor constant, we used a tube furnace equipped with an electronic PID-controller. The volume of the catalyst loaded into the reactor was 100 cm³, and the feed hourly space velocity was 400 h⁻¹.

The compositions of the initial *iso*-butane fraction and the contact gas were determined via gas chromatography. The content of hydrocarbons was determined on a GKh-1000 chromatograph (Khromos, Dzerzhinsk) using a flame ionization detector and a capillary column, while the contents of H₂, CH₄, and CO were found using a thermal conductivity detector and a packed column. The relative error in determining the concentrations of the components did not exceed 10%. The indicators described below were calculated using the results from chromatographic analysis:

—the catalytic activity defined as the yield of *iso*-butylene per transmitted *iso*-butane and calculated using the formula

$$A = \frac{\omega_{i-C_4H_8}^{\text{cont.gas}} - \omega_{i-C_4H_8}^{\text{feed}}}{\omega_{i-C_4H_{10}}^{\text{feed}}} \times 100,$$

where $\omega_{i-C_4H_8}^{\text{cont.gas}}$ is the concentration of *iso*-butylene in the contact gas, wt %, $\omega_{i-C_4H_8}^{\text{feed}}$ is the concentration of

iso-butylene in the feedstock, wt %, and $\omega_{i-C_4H_{10}}^{\text{feed}}$ is the concentration of *iso*-butane in the feedstock, wt %; and

—the selectivity defined as the yield of *iso*-butylene per decomposed *iso*-butane and calculated using the formula

$$S = \frac{\omega_{i-C_4H_8}^{\text{cont.gas}} - \omega_{i-C_4H_8}^{\text{feed}}}{\omega_{i-C_4H_{10}}^{\text{feed}} - \omega_{i-C_4H_{10}}^{\text{cont.gas}}} \times 100,$$

where $\omega_{i-C_4H_{10}}^{\text{cont.gas}}$ is the concentration of *iso*-butane in the contact gas, wt %.

The catalyst grains' resistance to wear was determined by the mass fraction of the losses after one hour of catalyst wear under an air flow. The method is based on the destruction of the catalyst particles in the fluidized bed. The resistance to wear was calculated using the formula

$$M_n = \frac{m \times 100}{m_0},$$

where m_0 is the initial mass (g) of the tested catalyst with grain sizes of 40–200 μm, and m is the mass of this catalyst (g) after one hour of wear.

Batches of KDI-M catalyst were produced under production-line conditions. Pilot tests of KDI-M were performed in a reactor unit for *iso*-butane dehydrogenation (Nizhnekamskneftekhim). Pilot batches of KDI-M were loaded into the reactor units along with IM-2201 catalyst. The total mass of the catalysts circulating in each reactor unit was approximately 300 t. The dehydrogenation of *iso*-butane was performed according to regulations at temperatures of 560–580°C, a pressure of 1.6 kgf/cm², and a feed loading of $\nu = 25\text{--}35$ t/h. The catalyst was regenerated at a temperature of 650°C and an air flow rate of 14000 m³/h. The composition of the initial *iso*-butane fraction was (wt %) C₃ hydrocarbons, 0.5–1.0; *iso*-butane, 93–95; *n*-butane, 0.5–2.0; *iso*-butylene, 2.0–4.0; *n*-butenes, 0.2–1.2; and 1,3-butadiene, 0.01–0.05. The operating indicators of IM-2201 (activity and selectivity) met the requirements of TU 2173-017-73776139–2009.

RESULTS AND DISCUSSION

The comparative characteristics of IM-2201, KDI, and KDI-M, determined on the laboratory unit, are given in the table.

The catalytic indicators of KDI-M were, on average, 1–2% higher than those of KDI. This improvement was achieved by modifying the aluminium oxide support with silicon dioxide before applying the active component and the promoter. The spread of the modifying agent in the form of SiO_x fragments over the support promotes the formation of the most active (in dehydrogenation) phase of polynuclear Cr(III) ions and the shielding of strong acidic centers of the sup-

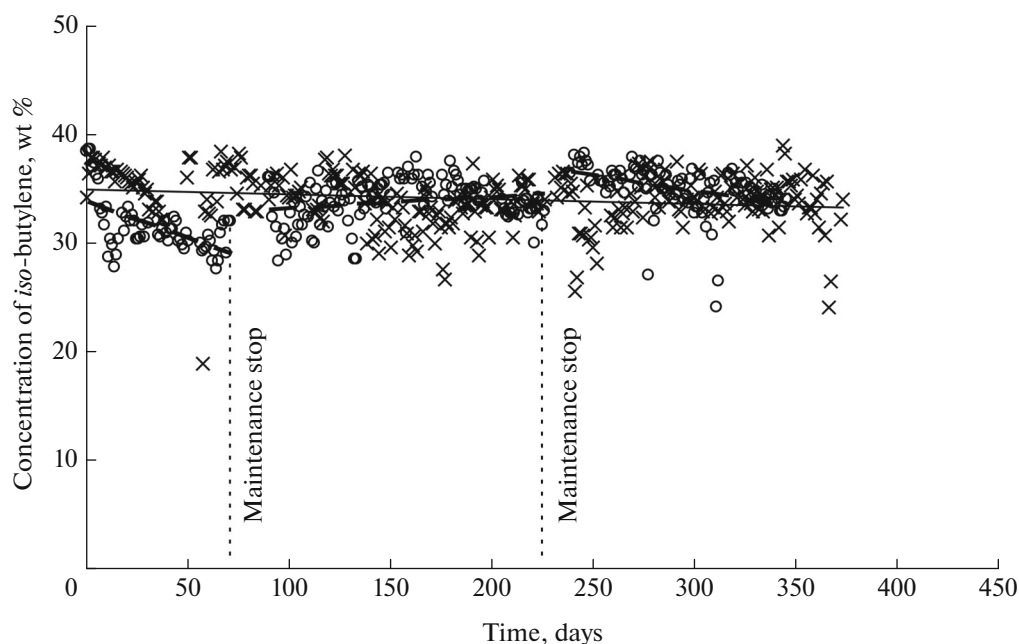


Fig. 1. Concentration of *iso*-butylene in the contact gas versus operating time of catalyst mixtures (○) IM-2201 + KDI and (×) IM-2201 + KDI-M.

port. This increases the activity and selectivity of the catalyst in the dehydrogenation of *iso*-butane [20].

In developing the technology for the production of KDI-M catalyst, we considered the results from laboratory studies and the accumulated experience in the industrial use of the KDI catalyst in the large-scale units of PAO Nizhnekamskneftekhim. For example, it was found in [18] that the optimum circulation of the catalyst in the reactor unit can be achieved by loading impregnation-type catalyst in the form of grains less than 40 μm in size and maintaining the content of these grains in the catalyst at a level of 30 wt %. It was shown in [19] that in order to stabilize the required level of the fluidized bed and lower the loss of the catalyst, the fraction of 20–40- μm grains in the circulating catalyst should be no less than 20 wt %. In light of the above requirements, a mathematical model of the destruction of IM-2201 and KDI during their use in large-scale reactors was constructed based on experiments on prolonged wear of the catalysts in a fluidized bed [21]. The model allowed us to establish the optimum resistance to wear and the grain-size composition of the loaded KDI-M catalyst. These optimum parameters promote the formation of the required amount of grains with sizes of less than 40 μm at a sufficient rate. They thus enhance the circulation of the catalyst and promote the formation of a stable and uniform fluidized bed and its required extension to the upper layers of the reactor.

The production of the developed KDI-M catalyst began in Nizhnekamsk in 2014. Batches of this catalyst that were produced specifically for the pilot testing

were loaded into the *iso*-butane dehydrogenation unit (Nizhnekamskneftekhim).

To assess the effect of the KDI-M catalyst on the operation parameters of the *iso*-butane dehydrogenation unit and the stability of its functioning, we ran a pilot test for one year. During the test, on a periodic basis of five to nine days, one of the two parallel units for *iso*-butane dehydrogenation was simultaneously loaded with the IM-2201 catalyst and batches of KDI-M in amounts of six to eight tons. The total monthly load of the KDI-M catalyst in the unit was raised from 10–15 t (at the initial stage) to 60 t in the latter half of the pilot test. For comparison, the parallel unit was loaded with a mixture of catalysts KDI and IM-2201 in a ratio of 50 : 50. Figures 1–3 show the changes in the concentrations of *iso*-butylene and $\text{C}_1\text{--C}_3$ hydrocarbons in the contact gas and the total catalyst consumption per ton of produced *iso*-butylene.

The pilot test showed that the use of the KDI-M catalyst in combination with IM-2201 is more effective than that of the IM-2201 + KDI mixture. The combination of IM-2201 and KDI-M ensured a stable yield of *iso*-butylene over 400 days of nonstop operation. During our studies, the concentration of *iso*-butylene in the contact gas was 33–37 wt %, 3–4% higher than the respective parameter determined for the IM-2201 + KDI mixture at the initial stage of pilot testing (see Fig. 1). In addition, the reactor unit loaded with the IM-2201 + KDI mixture was stopped for maintenance twice (after 72 and 132 days of operation) as a result of (a) loss of catalyst circulation between the

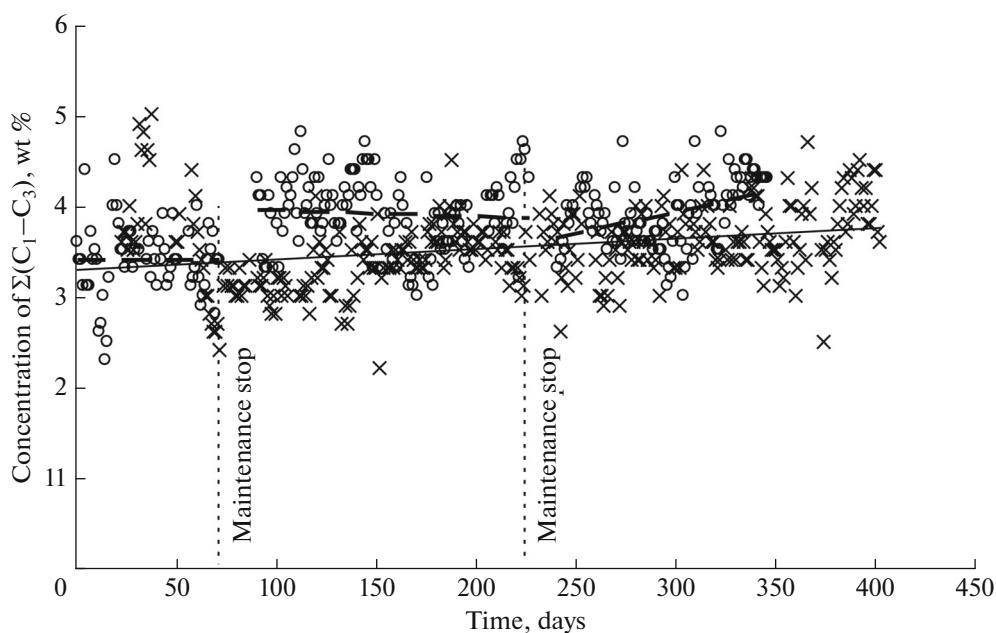


Fig. 2. Concentration of C_1-C_3 hydrocarbons in the contact gas versus operating time of catalyst mixtures (○) IM-2201 + KDI and (×) IM-2201 + KDI-M.

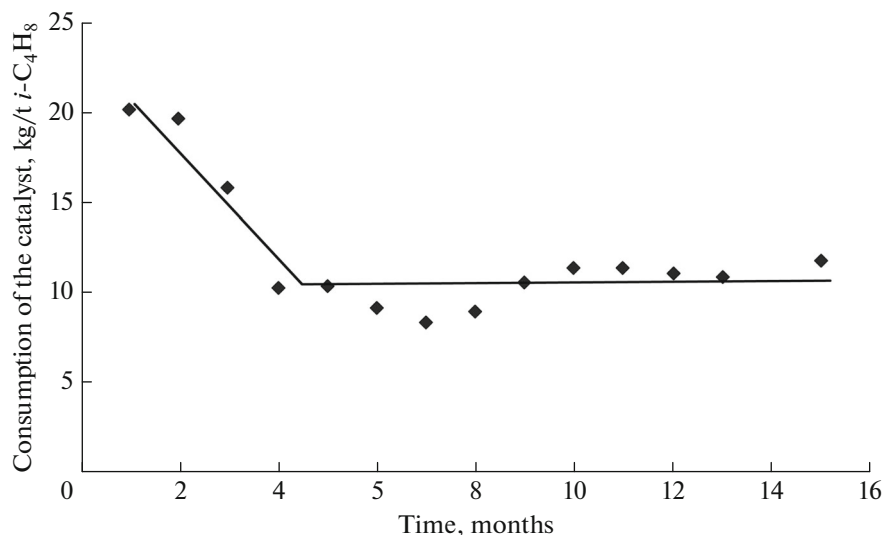


Fig. 3. Changes in the consumption of the catalyst per ton of *iso*-butylene produced in pilot testing.

reactor and the regenerator and (b) the reactor down-comer being blocked by coke.

Analysis of the trends of the dependence of the *iso*-butylene concentration showed that the operation of the IM-2201 + KDI-M mixture was more stable: over 400 days, the *iso*-butylene concentration in the contact gas fell by 5 rel %: on average, the value fell from 35 to 33 wt %. As for the IM-2201 + KDI mixture, the *iso*-butylene concentration in the contact gas fell by 12–14 rel % over 70–110 days (see Fig. 1).

The use of KDI-M catalyst instead of KDI thus not only increased the yield of *iso*-butylene but also increased the duration of the nonstop operation of the unit from 270 (for the mixture of IM-2201 and KDI) to 400 days. This was due to the stable dehydrogenation activity of the KDI-M catalyst, its low abrasiveness, and optimum grain-size composition, which enhances the circulation of the catalysts and makes it possible to decrease the supply of carrier gases. This in turn reduces the mechanical wear on (a) the internal

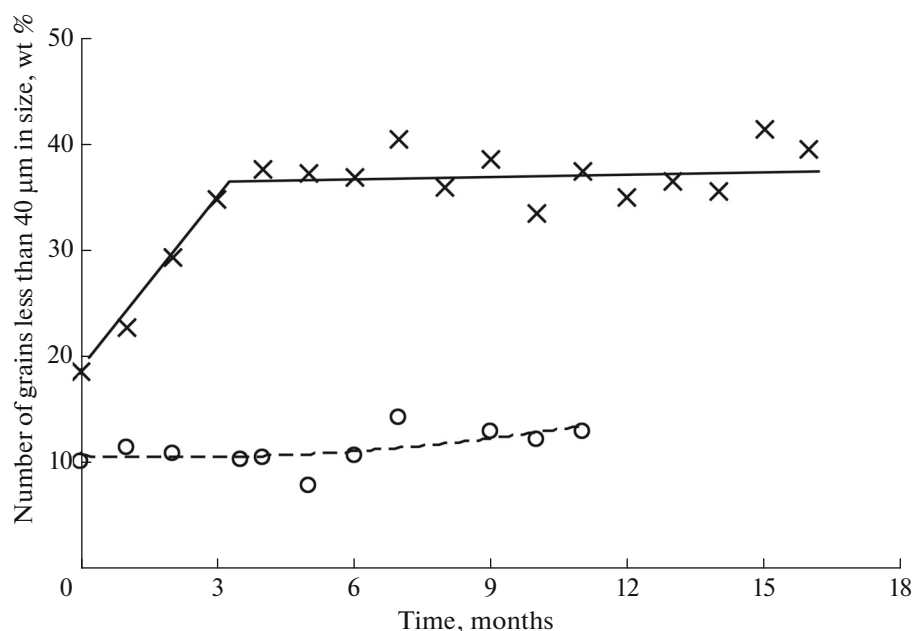


Fig. 4. Impact of the service life on the number of grains less than 40 μm in size in catalyst mixtures (○) IM-2201 + KDI and (×) IM-2201 + KDI-M.

components of the reactor and (b) the flow channels between the reactor and the regenerator.

When KDI-M is used in combination with IM-2201, the concentration of C_1 – C_3 hydrocarbons remains stable (at 3.5–4.0 wt %, 0.5–1.0 wt % lower than for the mixture of IM-2201 and KDI) over the period of operation (see Fig. 2).

The use of KDI-M catalyst, which is more durable than IM-2201, contributed to the lighter wear on the grains, the formation of particles less than 20 μm in size, and their carryover from the reactor via cyclones. As a result, the total consumption of the catalyst fell from 30 to 11–12 kg per ton of produced *iso*-butylene (see Fig. 3).

The use of KDI-M catalyst also led to the formation of 2.5–3 times as many grains less than 40 μm in size, compared to KDI catalyst (Fig. 4). At the initial stage of KDI-M loading, the content of grains less than 40 μm in size grew from 20 to 30–35 wt % and remained at this level. When a mixture of IM-2201 and KDI was used, the content of grains less than 40 μm in size did not exceed 20 wt %. The formation of the required number of such grains was ensured by the optimum grain-size composition of the initial KDI-M catalyst and the technological features of its production.

CONCLUSIONS

(1) A pilot test showed that as a result of loading KDI-M catalyst in combination with the circulating IM-2201 catalyst in the large-scale unit for *iso*-butane dehydrogenation, the concentration of *iso*-butylene in

the contact gas stabilizes at 33–37 wt % and the yield of C_1 – C_3 hydrocarbons falls by approximately 1 wt %.

(2) The use of the KDI-M catalyst prolongs the nonstop operation of the reactor unit from 270 (for the mixture of IM-2201 and KDI) to 400 days because of the stable dehydrogenation activity and grain-size composition of the circulated catalyst.

(3) The use of KDI-M reduced the total catalyst consumption per ton of produced *iso*-butylene from 30 (for IM-2201) to 11–12 kg because of the lighter wear on its grains.

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