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CATALYSIS

Dehydration of Isobutane in Fixed Bed on the Stable to Carbon Deposition Chromia-Alumina Catalysts

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Abstract—Study of chromia-alumina catalysts obtained from products of a thermochemical activation of aluminum trihydroxide for fixed-bed dehydrogenation of light paraffin hydrocarbons demonstrated that an increase in activity is observed in dehydrogenation of isobutane at a temperature of 590°C during the first 30 min of the catalytic process and then the activity slightly decreases. It was shown that the amount of carbon-deposition products on the surface of the synthesized catalysts after 120 min of isobutene dehydrogenation is 1–2 wt %. One of reasons for the high stability of chromia-alumina catalysts against carbon deposition is their porous structure. The use of the proposed catalysts in industry can improve the efficiency of the paraffin dehydrogenation processes by increasing the time of the reaction, while regeneration time is reduced.

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The processes of dehydrogenation of paraffin hydrocarbons are of high industrial importance to obtain a wide range of unsaturated hydrocarbons, including propylene, normal and iso-structural C_4–C_5 olefins, styrene, etc. [1]. Chromia-alumina catalysts have found application in direct [2–7] and oxidative [8–10] dehydrogenation of paraffins into the corresponding olefins. In Russia, the dehydrogenation of paraffins is mostly performed in a fluidized bed with microspherical catalysts of AOK 73-24, IM-2201, KDM, and other brands [11–14]. Performing the dehydrogenation in a fixed catalyst bed is believed to be more efficient because this provides a higher yield of unsaturated hydrocarbons, the catalysts has a longer service life, and there is no carryover of a substantial amount of the catalyst by the gas flow of reagents in view of its zero abrasion [15, 16]. However, one of the main problems for the fixed-bed catalyst, as also for a boiling-bed catalyst, is the loss of activity due to the carbon deposition processes [17]. Therefore, the dehydrogenation in a fixed bed, including the Catofin process, is performed in the cyclic mode, which includes the reductive activation with hydrogen (occasionally, there is no such stage), dehydrogenation, and oxidative regeneration. Between these stages, a catalyst is subjected to a vacuum treatment, or blowing with an inert gas [18]. According to data from different sources, the dehydrogenation stage takes 4 to 12 min, with the total duration of the activation–dehydrogenation–regeneration cycle being 25–30 min [19]. One of promising ways to improve the process efficiency is by making longer the dehydrogenation stage. This can be achieved by raising the catalyst stability against carbon deposition, with the catalyst necessarily retaining high conversion and selectivity parameters for providing a high yield of the product, unsaturated hydrocarbons. In industrial implementation of the dehydrogenation process this will require some additional procedures aimed to maintain a sufficiently high temperature of the catalyst bed under the conditions of the endothermic dehydrogenation reaction. This problem is partly solved by using an additional heat-generating material, which is charge in the Catofin process together with the catalyst and the inert diluent [20, 21].

In this regard, the purpose of this work was to develop a chromia-alumina catalyst stable to formation of carbon depositions to increase the time of the dehydrogenation step. Chromia-alumina catalysts were prepared on the basis of domestic raw materials, products formed in thermochemical activation of aluminum trihydroxide

(TCA ATH), and their catalytic properties and deactivation in the reaction of isobutane dehydrogenation in a fixed bed were examined.

EXPERIMENTAL

For comparison, we studied two chromia-alumina catalysts formed from products of thermochemical activation of aluminum trihydroxide. According to [22], the catalyst of the Catofin process contains the following components (wt %): CrO_3 17–24, Na_2O 0.1–0.3, K_2O 0.1–2, and ZrO_2 up to 1.5. We synthesized two catalysts with chemical composition close to that of the Catofin catalyst (wt %): Cr_2O_3 20, K_2O 2, and ZrO_2 1. Catalyst 1 was produced by the incipient wetness impregnation of TCA ATH preliminarily molded as cylindrical granules 2.7–3.0 mm in diameter and calcined at 700°C. The impregnation was made with an aqueous solution of chromium anhydride, potassium hydroxide, and zirconyl nitrate, all of chemically pure grade. Then the samples were dried at a temperature of 120°C for 4 h and calcined at 700°C for 4 h.

Catalyst was produced by wet mixing. For this purpose, TCA ATH was mixed in a mixer with *Z*-shaped blades with an aqueous solution containing a prescribed amount of dissolved precursors of chromium oxide, potassium, and zirconium. The resulting mass was molded by extrusion to give granules of similar size. The catalyst was dried at 120°C for 4 h and calcined at 700°C for 4 h. This way to obtain the catalyst is interesting and more profitable because of including the minimum number of technological procedures and involves only a single high-temperature treatment, in contrast to the impregnation method in which first the support is calcined and then the catalyst.

The characteristics of the porous structure were studied by the method of low-temperature adsorption of nitrogen on a Micromeritics Tristar 3020 instrument (United States). The specific surface area was determined by the BET method from the rectification of the adsorption isotherm at relative pressures in the range 0.05–0.30. The pore size distribution was constructed by using the BJH method from the desorption branch of the isotherm.

The catalytic properties of the catalysts synthesized in the study were examined in the reaction of isobutene dehydrogenation at a temperature of 590°C in a flow-through catalytic installation with a quartz reactor (inner diameter ~15 mm). The temperature was chosen because the dehydrogenation process is performed in the temperature range 540–600°C, but the processes of catalyst deactivation as a result of the carbon deposition have the highest intensity at 590°C and more. A 1-g portion of the catalyst (0.5–1-mm fraction) was mixed with an inert diluent, quartz glass of the same fraction in a 1 : 1 ratio. The reaction products were analyzed with a Khromatek-Kristall 5000.2 gas chromatograph. The components formed in the dehydrogenation of isobutene were separated on a Varian Capillary Column CP-Al_2O_3/Na_2SO_4. The main activity parameters of the catalyst: conversion *X* (vol %), selectivity *S* (%), and yield *Y* (%), were calculated by the formulas

$$X = 1 - \frac{c^{\text{out}}(i\text{-C}_4\text{H}_{10})}{c^{\text{in}}(i\text{-C}_4\text{H}_{10})} \times 100,$$

$$S = \frac{\Sigma c(\text{C}_4\text{H}_8)}{1/2\,[c(\text{C}_2\text{H}_6) + c(\text{C}_2\text{H}_4)] + c(\text{C}_3\text{H}_8) + c(\text{C}_3\text{H}_6) + \Sigma c(\text{C}_4\text{H}_8)} \times 100,$$

$$Y = \frac{SX}{100}.$$

A thermal analysis was made on an STA 449 F1 Jupiter analyzer (Netzsch-Geraetebau GmbH) in the DSC–TG mode in a flow of air (50 mL min^{-1}). The gas mixture composition in the burning of carbon on the catalyst surface was determined with a QMS 403D Aeölos mass spectrometer.

RESULTS AND DISCUSSION

The porous structure of the catalysts obtained on the basis of TCA ATH products was examined by the method of low-temperature adsorption of nitrogen. The table lists values of the specific surface area and pore volume for the

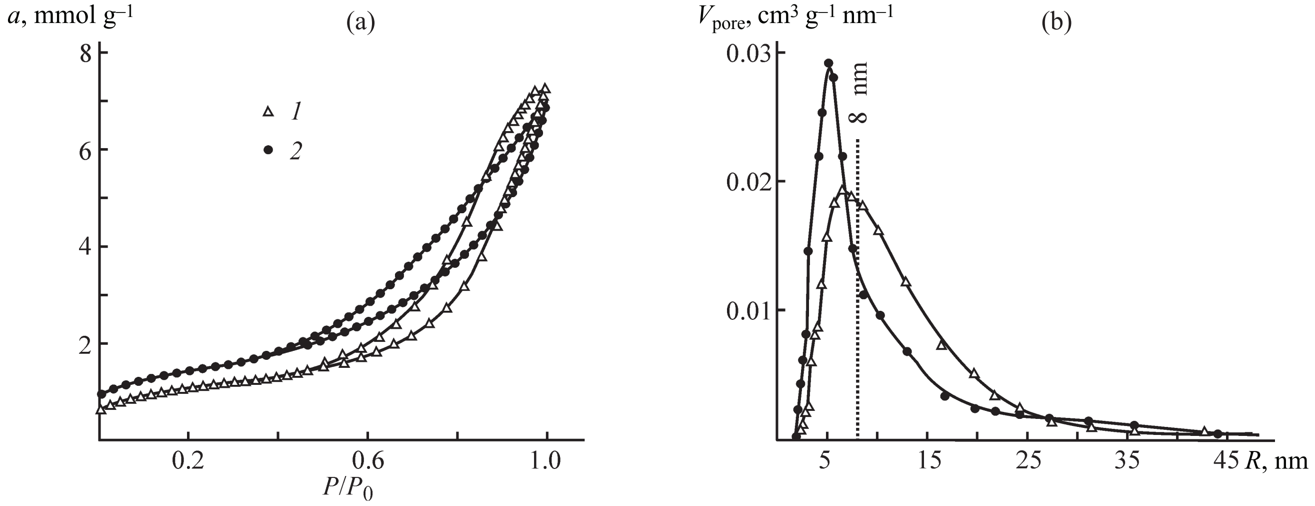

Fig. 1. (a) Isotherms of adsorption–desorption a of nitrogen and (b) pore size R distribution for the catalysts under study. (P/P_0) Relative pressure and (V_{pore}) pore volume.

catalysts we synthesized. Catalysts 1 and 2 have specific surface areas of 82 and 111 m^2 g^{-1} at pore volumes of 0.25 and 0.24 cm^3, respectively. The nitrogen adsorption–desorption isotherms and the pore size distributions for the samples are shown in Fig. 1. The nitrogen-adsorption–desorption isotherms (Fig. 1a) characteristically have a hysteresis loop at relative pressures in the range 0.5–1.0, which indicates that the catalysts have a mesoporous structure. For the catalyst 1 obtained by the impregnation method, the hysteresis loop is shifted to a large relative pressure range, indicating a large mesopores contribution to the porous structure of the sample. It can be seen from the pore size distributions (Fig. 1b) that a bimodal pore size distribution is observed for catalyst produced by mixing: there are pores 2–8 nm in size and pores larger than 8 nm. For catalyst 1, produced by impregnation of a preliminarily molded and calcined aluminum oxide, the pore size distribution is more strongly shifted to large sizes (>8 nm), which may be due to the partial dissolution of the alumina support in the course of impregnation with the acid solution of chromic acid. Thus, the catalysts based on TCA ATH have a lager specific surface area and pore volume. The micropore volume estimated by the t-plot method is insignificant for both the catalysts (see table), but is two times larger for catalyst 2. This may be due both to the more significant pore size redistribution for the impregnated catalyst in the repeated calcination and reprecipitation of the support in the presence of chromic acid (pH < 0) and to the distribution of chromium oxide within micropores of the support.

Figure 2 shows time dependences of the conversion and selectivity of the catalysts in the reaction of isobutane dehydrogenation at a temperature of 590°C. Catalysts 1 and 2 are characterized by an initial isobutane conversion of about 53.9 and 56.4%, respectively, at a selectivity of 93–95%. These data are close to the activity of the industrial catalysts for the Catofin process characterized by an initial isobutane conversion of 55.3–56.1% at a selectivity with respect to isobutylene of 91.5–92.1% for the process performed at a pressure of 0.33 atm [22].

Catalyst 2 produced by the mixing method is characterized by high conversion of isobutane at 15th min of dehydrogenation at a selectivity with respect to isobutylene of 93.5%. During the first 60 min of dehydrogenation, an insignificant decrease in the conversion is observed

Texture characteristics of the catalysts under study

Catalyst	S_{BET}, m^2 g^{-1}	V_{pore}, cm^3 g^{-1}	Volume of >8-nm pores		V_{micro}(t-plot), cm^3 g^{-1}
			cm^3 g^{-1}	%	
1	82	0.25	0.177	70.4	0.004
2	111	0.24	0.117	49.8	0.008

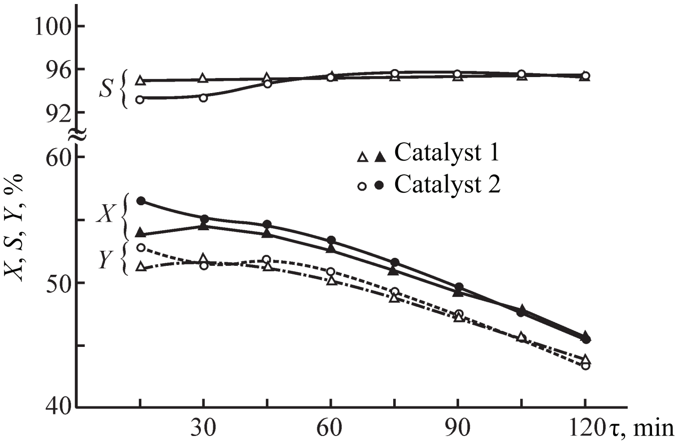

Fig. 2. Isobutane conversion *X*, selectivity *S* with respect to isobutylene, and isobutylene yield *Y* vs. time τ for the catalysts under study in the dehydrogenation of isobutane at 590°C.

and the selectivity increases from 93.5 to 95.6%, with this value preserved during the second hour of dehydrogenation. The increase in the selectivity may be due to the blocking of a part of active centers of the catalyst, supposedly strong acid centers, by carbon deposition processes. As a result, the conversion of isobutane somewhat decreases, with the selectivity for the target process increasing. During the second hour of dehydrogenation, a more intense deactivation of the catalyst is observed, with the conversion of isobutane decreasing from 56.4 to 45.5%. The advisability of performing the dehydrogenation during the second hour is determined by the yield of isobutylene, which decreases from 50.8 to 43.4% during the period from 60th to 120th min of dehydrogenation.

Catalyst 1, produced by the impregnation method, exhibits in the initial period of time a lower conversion of isobutane, compared with catalyst 2. However, its activity (conversion of isobutane) slightly increases by 30th min of dehydrogenation and becomes comparable with the conversion for catalyst 2. The increase in the activity of the catalyst is indicative of its development in the course of isobutane dehydrogenation, which may be due to the after-reduction of Cr(VI) to Cr(III) by the reaction mixture to give an additional number of active centers. Catalyst 1 also has a high stability, and in its subsequent dehydrogenation, the conversion of isobutane decreases from 54.6 to 46%. The selectivity with respect to formation of isobutylene is higher for the impregnated catalyst, compared with catalyst 2, and insignificantly grows during the dehydrogenation (from 94.9 to 95.5%).

Thus, catalysts based on TCA ATH are characterized by a high catalytic activity in the dehydrogenation of isobutane, which is comparable with activity of industrial catalysts, but have a higher selectivity and are weakly deactivated in the course of a prolonged dehydrogenation.

To examine the carbon deposition products after 120 min of dehydrogenation, we cooled the catalysts, instead of performing the subsequent oxidative treatment, in the catalytic reactor to room temperature in a flow of inert gas (nitrogen). Then, an approximately 10-mg portion of a homogenized catalyst sample was examined by the DSC–TG method, with mass-spectrometric monitoring of gaseous products. Figure 3 shows the data obtained with the catalysts heated in a flow of air at a rate of 10 deg min^{-1}. The catalysts exhibit a loss of mass in the temperature range 250–450°C, accompanied by an

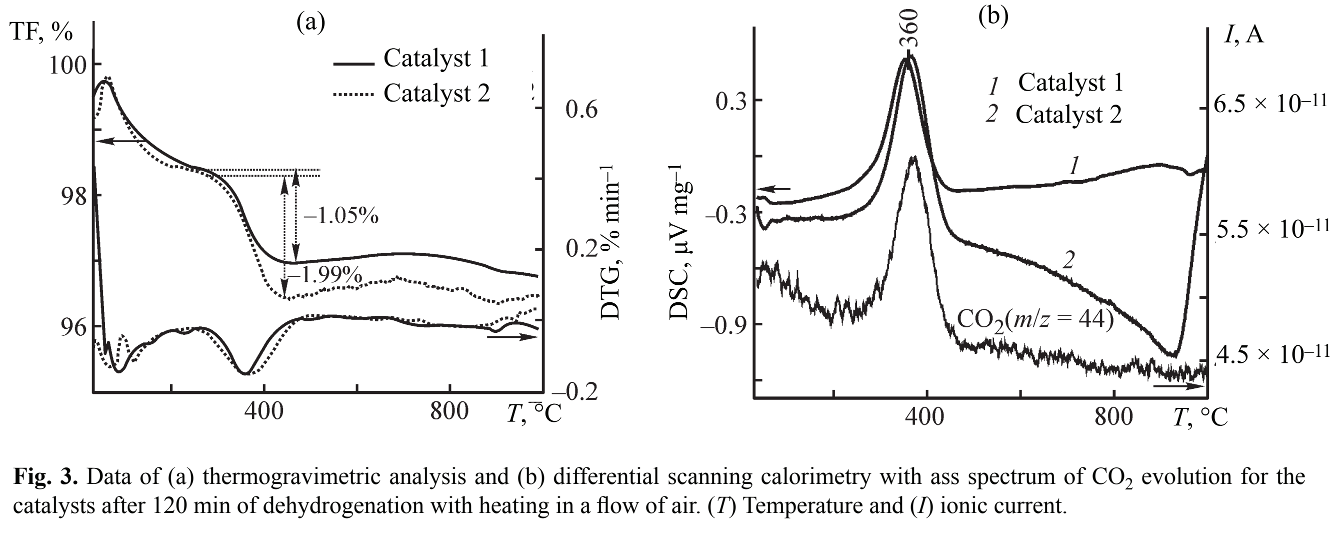

Fig. 3. Data of (a) thermogravimetric analysis and (b) differential scanning calorimetry with ass spectrum of CO_2 evolution for the catalysts after 120 min of dehydrogenation with heating in a flow of air. (*T*) Temperature and (*I*) ionic current.

exothermic effect and evolution of CO_2 (Fig. 3b), which indicates that carbon burns on the catalyst surface. The close temperature range and the nature of the loss of mass point to the about the same nature of carbon deposits formed on the catalysts under study. At the same time, the amounts of mass lost by the catalysts differ significantly: for catalyst 2, produced by the mixing method, the loss of mass is 1.99%, and that for catalyst 1 is 1.05%. These data are in good agreement with the data obtained in a study of the operation stability of the catalysts in the dehydrogenation of isobutane. Catalyst 1 shows the highest selectivity and stability, and, accordingly, the amount of carbon deposition products formed on its surface is lower.

CONCLUSIONS

Two chromia-alumina catalysts based on products formed in thermochemical activation of aluminum trihydroxides and close in chemical composition to the industrial catalyst for the Catofin process were compared in the reaction of isobutane dehydrogenation. The catalysts have a high catalytic activity that is comparable with the activity of the industrial catalyst, but show a higher selectivity with respect to isobutylene. The catalysts synthesized in the study are insignificantly deactivated during 60 min of dehydrogenation, whereas the industrial catalyst for the Catofin process is operative during 4–12 min. The high stability of the catalysts can be used to raise the efficiency of the process in which light paraffin hydrocarbons and, in particular, isobutane are dehydrogenated due to the longer duration of the dehydrogenation stage.

The method of a thermogravimetric analysis demonstrated that the amount of carbon-deposition products formed during 120 min of dehydrogenation is 1–2% relative to the catalyst mass. The burning-out of carbon occurs at comparatively low temperatures, 250–450°C, whereas in the industry, the oxidative regeneration process is performed at 650°C. Accordingly, it is expected that the time of the catalyst regeneration step can be reduced. It will also increase the efficiency of the dehydrogenation process. In this case, the occurrence of the exothermic reaction of burning of carbon deposits leads to heating of the catalyst bed in the regeneration stage, which is used in the industry to maintain a high temperature in the catalyst bed at a minimum external delivery of heat.

One of the main reasons why the selectivity and stability of the catalysts obtained in the study is the special porous structure of the catalysts, produced because products of a thermochemical activation of aluminum trihydroxide are used as a precursor of the support. When catalysts are synthesized by different methods, catalyst 1 with smaller specific surface area is comparable in activity with catalyst 2 and is more stable due to the more pronounced contribution of large mesopores (>8 nm), which favor an effective delivery of reagents to the active centers of the catalyst and removal of reaction products.

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