Study of the Stability of the Gallium-Containing Catalyst in the course of Conversion of Gaseous C₁-C₆ Hydrocarbons into Aromatic Compounds

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Abstract. A study was made on the duration of the single-pass lifespan of the gallium-containing catalyst in the course of conversion of a model mixture of C₁-C₆ hydrocarbons into aromatic compounds. Using temperature-programmed desorption of ammonia, it has been found that some acid sites of the catalyst were irreversibly deactivated as a result of the reaction and oxidative regeneration. It has been shown that the gallium-containing catalyst characterized by high activity and stability in the course of aromatization of lower alkanes was able to withstand a certain number of reaction-regeneration cycles without reducing its activity.

1. Introduction
Aromatic hydrocarbons are the most important feedstock for the production of valuable chemical products, such as high-octane components of motor fuels, plastics, plasticizers, synthetic resins and fibers, etc. The modern industrial production of aromatic hydrocarbons is based on the processing of petroleum fractions. Despite the fact that catalytic reforming is currently the main industrial process for producing aromatic hydrocarbons, the process of dehydroaromatization of light alkanes is also of great interest, as a process giving a higher yield of aromatic hydrocarbons compared with that of reforming. A significant role in this process is played by catalysts based on zeolites of the pentasil family, which are characterized by a regular pore structure and contain active sites of various natures [1-5]. The main properties of zeolite catalysts determining the effectiveness of catalytic processes are activity and selectivity to the target product. At the same time, the constancy of these characteristics over the longest possible time of operation of the catalysts is no less important but sometimes crucial. As a result of this, a very important task to increase the duration of the stable operation of the catalysts arises. Therefore, the determination of single-pass lifespan (inter-regeneration time) of the catalysts and the total number of reaction-regeneration cycles is of great importance from the point of view of the practical use of catalytic systems Our previous investigations showed the promise of using pentasil catalysts modified with gallium via hydrothermal synthesis in the dehydroaromatization reaction of lower C₃-C₄ alkanes [6-7]. The main direction of the process running over such catalysts is aromatization. As a result, more than 50% of aromatic hydrocarbons, mainly benzene, toluene, and xylene could be obtained from the propane-butane mixture. Studies of the behavior of catalysts directly in the course of conversion of real gaseous feed produced, for example, in oil fields, are of...
great research and practical interest. A wide fraction of light hydrocarbons (WLHF) is an example of these feed mixtures. These mixtures vary greatly in composition. This depends on the location of the oil field, the type of recoverable feed (oil or gas condensate), the degree of low-temperature separation, stage of separation, technological capabilities of oil treatment plants, etc. However, the delivery of gaseous feedstock from an oil field for investigation is usually associated with many difficulties, including the impossibility to pump it into a cylinder under high pressure. Usually, the pressure does not exceed 0.8 MPa, which does not allow conducting of extensive studies with long-term testing of catalysts and, especially, with a relatively high consumption of feedstock. The aim of this work was to study the duration of the gallium-containing catalyst in several inter-regeneration cycles during the conversion of the model mixture of C₁-C₆ hydrocarbons into aromatic compounds.

2. Materials and methods
The object of the study was a gallium-containing zeolite of the structural type MFI (SiO₂/Al₂O₃ + Ga₂O₃ = 40, the content of Ga₂O₃ in the reaction mixture was 2.2 wt%) prepared by hydrothermal crystallization of alumina-silica gel, where part of the aluminum was substituted with gallium, with the addition of 20% of binder (pseudooboehmite).

A model mixture of C₁-C₆ hydrocarbons was used as the feedstock (wt%: methane – 8.4; ethane – 12.8; propane – 38.9; i- and n-butane – 17.0 and 19.0, respectively; pentane and above – 3.9). The catalyst was tested in an OL-120 flow-circulation unit with a reactor volume of 100 cm³ at the following process parameters: temperature range – 450-600 °C, bulk feed rate – 170 h⁻¹, pressure – 0.1 MPa. The reaction products were analyzed by GLC using a Chromatec-Crystal 5000.2 chromatograph. The acidic properties of Ga-containing zeolite catalysts were studied by temperature-programmed desorption of ammonia. The strength of acid sites of the catalyst was estimated from the temperature maxima on the thermal desorption curve, their concentration was determined from the amount of ammonia desorbed at the moment of fixation of the desorption peaks. It was expressed in μmol per 1 g of catalyst.

The nature of the coke deposits forming on the catalyst surface during alkanes C₁-C₆ aromatization was studied on a Q-1500 thermal analyzer (MOM, Hungary). Thermoanalytical data were processed using the T-analiz software, which ensured sample temperature and heating rate control and measurement and simultaneous recording of the sample weight (TG) and thermal events (DTA). The heating rate was 10°C/min, and the initial sample weight was 400 mg. Thermal analyses were carried out in air. The reference sample was α-Al₂O₃.

The carbonized catalyst was regenerated according to a specially developed technique as follows: after the catalyst was completed, the reactor heated to the final reaction temperature was purged with an inert gas (nitrogen) with a feed rate of 100 h⁻¹ for 30 min until the hydrocarbon components adsorbed on the catalyst were completely removed, and then the reactor was cooled to a temperature of 450 °C and purged with nitrogen for another 30 minutes. After that, regeneration of the catalyst with a nitrogen-air mixture was started by stepwise raising the temperature to 550 °C. The step was 10 °C and the initial oxygen concentration in the mixture was 0.5% vol. The oxygen step in the mixture was 0.5% vol. The composition of the exhaust gas mixture was controlled using a gas chromatographer. Then, the oxygen concentration in the nitrogen-air mixture was increased to 5% vol. at a constant temperature. After reaching a 5% oxygen content in the regeneration mixture, the oxygen step was increased to 2% vol. The oxygen content was adjusted to its content in air (~ 21 vol. %), while the reactor temperature was maintained constant. The catalyst was calcined in air stream (space velocity of air supply 100 h⁻¹) for 6 h at a temperature of 550 °C. In the case of a high degree of carbonization of the catalyst, the temperature in the reactor was raised to the maximum possible value of 600 °C, and the catalyst was calcined in air stream for another 4 hours. After a regeneration cycle, the reactor was purged with inert gas for 60 min and its temperature was reduced to 450 °C. Then the nitrogen supply was stopped and the initial mixture of C₁-C₆ alkanes was passed through the catalyst bed.
3. Discussion

Table 1 presents the results of studies, which show that the total activity and stability of the Ga-containing zeolite catalyst slightly increase from cycle to cycle. During the first reaction cycle, the catalyst worked stably for 34 hours. It exhibited high aromatization activity already at the beginning of the process, which then increased slightly with a rise in temperature to 520-540 °C. A slightly different picture was observed during the second single-pass lifespan; hence, in the initial period of the reaction the catalyst exhibited a lower activity than during the first cycle, but as it worked with increasing temperature, the conversion and yield in aromatic hydrocarbons increased. After 34 hours of continuous operation, the catalyst continued to operate stably for the next 24 hours, the conversion of the feedstock was more than 65%, and the yield in aromatic hydrocarbons was about 40%. After the next oxidative regeneration, the time of stable operation of the zeolite-containing catalyst increased by another 10 hours, while the sample showed the highest catalytic activity during the 3rd reaction cycle. This indicates that during the reaction and from cycle to cycle under the influence of the reaction medium, the effect of ‘development’ of the catalyst was observed as a result of the transition of the promoting element to the active electronic state (Ga$^{1+}$) which has given a higher aromatization activity to the catalyst.

In Figure 1 the dependences of the selectivity to the formation of aromatic hydrocarbons over a Ga-containing zeolite catalyst on the time of its operation in the course of 1$^{st}$, 2$^{nd}$, and 3$^{rd}$ inter-regeneration cycles are given. It is evident that the selectivity to the formation of aromatic hydrocarbons varied slightly from cycle to cycle; hence it was more than 50% after the catalyst has reached a stable level of operation. In addition, it can be noted that in the first hours of operation of the catalyst a noticeable increase in the selectivity of the formation of aromatic hydrocarbons was observed. This, apparently, is due to the fact that, under the influence of the reaction medium, the new proton acid centers were formed, which were highly active in the aromatization reaction of lower alkanes. After work for 178 hours over three reaction cycles, the catalyst remained active, so it might be used for subsequent cyclic tests in the course of aromatization of a mixture of lower C$_1$-C$_6$ alkanes.

![Figure 1. Selectivity to the formation of C$_6$+ aromatic hydrocarbons (1, 2, 3, respectively) vs the catalyst operating time during the 1$^{st}$, 2$^{nd}$, and 3$^{rd}$ inter-regeneration cycles in the course of the aromatization of C$_1$-C$_6$ alkanes](image-url)
Table 1. Main indicators of the process of conversion of a mixture of C<sub>1</sub>-C<sub>6</sub> alkanes over a Ga-containing zeolite during the time of its operation and from cycle to cycle

| T<sub>reaction</sub>, °C | τ, ч | X, % | A<sub>1</sub>, % | A<sub>2</sub>, % | A<sub>3</sub>, % | S, % |
|-------------------------|-------|------|----------------|----------------|----------------|------|
|                         | I operation cycle |       |                |                |                |      |
| 450                     | 2     | 35.2 | 17.7           | 1.4            | 78.2           | 50.3 |
| 460                     | 4     | 42.5 | 25.6           | 1.3            | 70.0           | 60.2 |
| 480                     | 6     | 55.2 | 34.0           | 1.7            | 61.5           | 61.6 |
| 500                     | 8     | 68.5 | 40.4           | 1.6            | 52.6           | 59.0 |
| 520                     | 16    | 76.4 | 46.0           | 1.2            | 45.7           | 60.2 |
| 540                     | 27    | 78.0 | 47.2           | 1.3            | 44.1           | 60.5 |
| 540                     | 34    | 81.3 | 42.4           | 2.0            | 49.1           | 59.5 |
| 560                     | 42    | 88.1 | 16.4           | 11.5           | 69.9           | 43.0 |
| 580                     | 46    | 92.3 | 7.3            | 8.7            | 80.4           | 32.7 |
| 600                     | 48    | 94.0 | 2.7            | 13.3           | 83.1           | 14.2 |
|                         | II operation cycle |       |                |                |                |      |
| 450                     | 2     | 31.2 | 17.6           | 2.0            | 77.4           | 56.4 |
| 460                     | 4     | 41.4 | 23.8           | 2.3            | 69.7           | 57.5 |
| 480                     | 6     | 52.5 | 31.8           | 2.7            | 60.6           | 60.6 |
| 500                     | 8     | 60.4 | 36.7           | 1.7            | 56.8           | 60.8 |
| 520                     | 16    | 67.8 | 42.6           | 1.6            | 49.5           | 62.8 |
| 520                     | 27    | 68.0 | 42.7           | 2.2            | 52.3           | 62.8 |
| 530                     | 34    | 69.4 | 45.0           | 2.4            | 46.6           | 64.8 |
| 540                     | 42    | 71.5 | 46.6           | 2.6            | 44.0           | 65.2 |
| 540                     | 46    | 68.8 | 43.8           | 3.1            | 46.9           | 63.7 |
| 540                     | 48    | 68.0 | 43.6           | 3.2            | 47.0           | 64.1 |
| 550                     | 52    | 68.1 | 43.4           | 3.3            | 47.0           | 63.7 |
| 560                     | 56    | 66.2 | 41.0           | 4.5            | 47.9           | 61.9 |
| 570                     | 58    | 65.1 | 39.6           | 5.2            | 48.9           | 60.8 |
| 580                     | 61    | 57.1 | 32.2           | 7.9            | 54.4           | 56.4 |
| 600                     | 62    | 51.6 | 25.1           | 13.6           | 57.4           | 48.6 |
|                         | III operation cycle |       |                |                |                |      |
| 450                     | 2     | 49.4 | 14.3           | 4.7            | 79.6           | 28.9 |
| 460                     | 4     | 51.2 | 21.3           | 4.5            | 72.4           | 41.6 |
| 480                     | 6     | 56.9 | 29.1           | 3.9            | 63.7           | 51.1 |
| 500                     | 8     | 64.5 | 33.8           | 3.2            | 58.8           | 52.4 |
| 520                     | 16    | 78.8 | 43.5           | 2.5            | 48.6           | 55.2 |
| 530                     | 27    | 79.9 | 45.1           | 2.2            | 46.9           | 56.4 |
| 530                     | 34    | 79.7 | 45.0           | 2.7            | 48.6           | 56.5 |
| 540                     | 42    | 80.0 | 46.8           | 2.7            | 44.2           | 58.5 |
| 540                     | 46    | 78.4 | 45.0           | 2.9            | 46.8           | 57.4 |
| 550                     | 52    | 75.3 | 43.8           | 3.1            | 47.0           | 58.2 |
| 550                     | 56    | 73.8 | 43.0           | 4.2            | 47.3           | 58.3 |
| 560                     | 61    | 71.7 | 40.2           | 5.9            | 47.8           | 56.1 |
| 570                     | 64    | 67.2 | 37.3           | 7.2            | 50.3           | 55.5 |
| 580                     | 66    | 61.8 | 32.4           | 7.9            | 55.1           | 52.4 |
| 600                     | 68    | 59.2 | 30.2           | 10.0           | 55.8           | 51.0 |

Note. τ is the operating time; X is the conversion; A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> are the yields in aromatic hydrocarbons, alkenes, and alkanes, respectively; S is the selectivity to the formation of aromatic hydrocarbons.
The acidic properties of a fresh catalyst, a sample after 2 cycles of operation, and a sample after 2 cycles of operation with subsequent oxidative regeneration are presented in Table 2. As can be seen from the data, the sample exhibited a noticeable decrease in the strength and concentration of acid centers of both types after 2 cycles of operation. However, the oxidative regeneration of the catalyst resulted in an almost complete reactivation of its acidic properties. Only a slight decrease in the total concentration of acid sites was observed, while the number of strong acid sites has decreased slightly, i.e. some of the acid sites were irreversibly deactivated as a result of the reaction and subsequent oxidative regeneration.

| Catalyst | $T_{\text{max}}$ °C | $T_{\text{I}}$ | $T_{\text{II}}$ | $C_{\text{I}}$ | $C_{\text{II}}$ | $C_{\Sigma}$ |
|----------|-----------------|------------|-------------|-------------|-------------|-------------|
| Fresh    |                 | 225        | 445         | 267         | 208         | 475         |
| After 2nd operating cycle | 215         | 390         | 190         | 103         | 293         |
| After 2nd cycle of operation and regeneration | 225        | 440         | 259         | 195         | 454         |

Note. $T_{\text{I}}$, $T_{\text{II}}$ – temperature of peak maximum for I and II catalyst forms and $C_{\text{I}}$, $C_{\text{II}}$ – concentration of acid sites in catalyst forms I, II, respectively; $C_{\Sigma}$ – total concentration.

At the same time, as can be seen from the data in Table 1, the catalytic activity and selectivity of the gallium-containing zeolite catalyst remained high and even grew from cycle to cycle, i.e. the sample contained a sufficient amount of acid sites necessary for aromatization of lower alkanes with a high selectivity. Apparently, first of all, surface acid sites that exhibited a high activity during the first reaction cycle were irreversibly deactivated, due to which the stability of the catalyst during the 1st reaction cycle was the lowest.

Thus, it is seen from the data on the catalytic and acid properties of the catalyst that as a result of the reaction-regeneration cycles, a slight decrease in the acidity of the catalyst has occurred, which, in turn, has led to an increase in its stability. It is possible that highly condensed carbon deposits have been formed and accumulated as a result of long-term operation of the catalyst. These deposits were not completely removed during oxidative regeneration, which has resulted in an irreversible deactivation of some of its acid sites.

A differential thermal analysis of a sample coked during the aromatization of a mixture of lower C$_1$-C$_6$ alkanes after the 2nd operation cycle has revealed the presence of overlapping exothermic effects within the region 450-760 °C with a clear peak at a temperature of 615 °C and a high-temperature shoulder, which suggests the presence of a wide range of coke deposit structures (Fig. 2). The total mass of coke deposits for 62 hours of catalyst operation during the 2nd reaction cycle was 7.6%. The catalyst, which worked during two cycles and underwent oxidative regeneration, contained no residual coke. The DTG and DTA curves show the presence of only one effect, i.e. the removal of water up to 300 °C with a maximum temperature at 115 °C. From the data of differential thermal analysis it follows that a complete coke removal occurs under the oxidative regeneration. It is likely that after 62 hours of catalyst operation no highly condensed molecules have been formed during the conversion of lower alkanes, since no coke has remained on it after regeneration. Therefore, a slight decrease in the acidity of the catalyst from cycle to cycle can be explained by structural changes that occurred at high temperatures in the zeolite crystal lattice under the influence of the reaction medium, and also, possibly, by a change in the composition of the catalytic system due to the gradual removal of extra-lattice gallium atoms during the reaction.
Figure 2. Thermograms of catalyst samples after 2nd cycle of operation (1) and regeneration (2)

The data of catalytic studies and thermal analysis point that in the course of oxidative regeneration, coke has been completely removed from the surface of the catalyst and its aromatic activity has been restored. Under optimal process conditions, a high conversion of C₁-C₆ gaseous hydrocarbons (about 80%) into a mixture of aromatic compounds (yield more than 40%, selectivity more than 50%) has been achieved. The mixture consisted mainly of benzene, toluene, xylene (BTX fraction), and naphthalene. The small amounts of C₉+ alkylbenzenes, methyl- and dimethylnaphthalenes were also present.

4. Conclusion
Thus, the studies showed the possibility of obtaining aromatic hydrocarbons from a mixture of C₁-C₆ alkanes using a catalytic system based on a structural galloaluminosilicate of the MFI zeolite. The catalyst retains high aromatization activity during the conversion of lower alkanes over a rather long period of work and it is able to withstand a relatively large number of oxidative regeneration cycles without reducing its catalytic activity.

Acknowledgments
This work was carried out as part of project No. V.46.2.1 of the Program for Fundamental Scientific Research of State Academies of Sciences.

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