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RESEARCH ARTICLE

Study into optimizing the temperature regime for the reduction of Fischer–Tropsch synthesis catalysts

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Abstract

Objectives. The work set out to investigate the potential for developing an efficient cobalt catalyst for Fischer–Tropsch synthesis through low-temperature activation by reduction in hydrogen directly in the synthesis reactor. Such an approach could be used to enhance the overall economic viability of the process.

Methods. The reduction of a zeolite-containing catalyst with a heat-conducting system based on thermally expanded graphite in an aluminum oxide binder carrier was investigated within the temperature range of 300–400°C. The degree of reduction of the powdered catalyst (to remove diffusion restrictions) was determined by conducting temperature-programmed reduction subsequent to the reduction at the studied temperature. Autosorb-1C and STA 449 F1 (*Netzsch*, Germany) devices were used in this work. The identified activation mode was evaluated at a Fischer–Tropsch synthesis pilot plant at *INFRA* (Moscow, Russia).

Results. Activity and selectivity values of the catalyst reduced at 325°C are determined from chromatographic analysis of the products. Low-temperature (325°C) reduction is shown to provide better catalytic parameters due to the implementation of a larger number of highly dispersed cobalt-oxide structures fixed on the hydrated surface of the support, resulting in the appearance of $Co^{\delta+}$ centers with increased activity and selectivity for the formation of C_{5+} hydrocarbons.

Conclusions. The described catalytic system demonstrates the potential advantages in carrying out reductive activation in hydrogen at 325°C as opposed to the conventional 400°C. This approach markedly enhances the economic viability of the entire process, particularly for small-scale installations, due to the reduced thermal stability of the steel material reactor.

Keywords

Fischer–Tropsch synthesis, cobalt catalyst, low-temperature reduction, thermally expanded graphite

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НАУЧНАЯ СТАТЬЯ

Исследование возможности оптимизации температурного режима восстановления катализаторов синтеза Фишера–Тропша

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Аннотация

Цели. Изучить возможность получения высокоэффективного кобальтового катализатора для синтеза Фишера–Тропша при низкотемпературной активации восстановлением в водороде непосредственно в реакторе синтеза с целью повышения общей экономической привлекательности процесса.

Методы. Восстановление цеолитсодержащего катализатора с теплопроводящей системой на базе терморасширенного графита в составе носителя с алюмооксидным связующим изучено для диапазона температур 300–400°C. Методом термопрограммированного восстановления, проводимого после восстановления при изучаемой температуре, определялась степень восстановления порошкообразного (для снятия диффузионных ограничений) катализатора. В работе использованы приборы Autosorb-1C и STA 449 F1 (*Netzsch*, Германия). Найденный режим активации испытан на опытной установке синтеза Фишера–Тропша в *ООО «ИНФРА»* (Москва, Россия).

Результаты. Представлены определенные из хроматографического анализа продуктов значения активности и селективности в синтезе Фишера–Тропша восстановленного при 325°C катализатора. Показано, что низкотемпературное (325°C) восстановление обеспечивает лучшие каталитические параметры за счет реализации большего количества закрепленных на гидратированной поверхности носителя высокодисперсных кобальт-оксидных структур, обуславливающих возникновение центров $Co^{\delta+}$ с повышенной активностью и селективностью образования углеводородов C_{5+}.

Выводы. Для исследованной каталитической системы показана возможность и желательность восстановительной активации в водороде при 325°C вместо стандартных 400°C. Это существенно повышает экономическую привлекательность процесса в целом, особенно для малотоннажных установок и в связи со снижением требований к термоустойчивости материала стального реактора.

Ключевые слова

синтез Фишера–Тропша, кобальтовый катализатор, низкотемпературное восстановление, терморасширенный графит

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INTRODUCTION

A substantial body of research and industrial experience with catalysts for Fischer–Tropsch synthesis (FTS) has demonstrated that their properties are contingent upon a number of factors, including the chemical and phase composition of the systems (including the realized porous structure), as well the conditions of formation, activation, and operation in the process.

The reduction procedure, which has historically been conducted on disparate equipment with subsequent loading of the operational system into the synthesis reactor or directly in the FTS reactor with selective conditioning, is of paramount importance for the efficient and economically viable production of hydrocarbons for a multitude of applications.

Depending on the nature and concentration of the active metal and the type of carrier, as well as the temperature (250–500°C) and reduction time, the volume and linear velocity of the gas and its composition vary from pure hydrogen to its mixtures with inert gas and CO_2, including direct activation in synthesis gas [1–11]. It is obvious that activation in synthesis gas can potentially reduce (in the case of sufficiently high catalytic activity) the costs of the FTS process. As noted in [12], synthesis gas reduction contributes to the formation of cobalt carbides (Co_xC, $x = 2, 3$), which improve activity by converting from carbides to metallic cobalt with a hexagonal close-packed (hcp) crystal phase. In other cases, inactive Co_xC blocks the active centers of the metal, leading to deactivation of the catalyst. The observed improvement in activity is largely due to an increase in the number of working cobalt centers due to the high dispersion of the metal; however, CO conversion and selectivity for the formation of C_{5+} remain significantly lower than in the presence of a catalyst reduced in pure hydrogen. As found for the model Co/SiO_2 catalyst offering a relatively weak metal-carrier interaction [13], the structural parameters of cobalt previously reduced in hydrogen do not significantly change due to aggregation up to 500°C. At the same time, the presence of CO in the reducing gas leads to the formation of carbonaceous compaction products on the metal surface (at 300–500°C), which reduce the availability of reactants for catalysis.

High-performance catalysts for FTS with thermally conductive additives in the form of flaked aluminum [14], carbon fiber or thermally expanded graphite [15–17] may differ significantly from each other in terms of activation conditions that should be developed for specific systems.

The interaction of a catalytically active metal and its precursors with carriers of various natures is a complex phenomenon that gives rise to a number of effects. The crucial presence in this process of an aluminum oxide binder (boehmite and pseudoboehmite) plays a role in the formation of granules with distinctive properties. These differences are attributed to the varying chemical structures and the manner in which substances are produced by different manufacturers. As shown by the example of the reduction of catalysts with a thermally conductive network of metallic aluminum [18], the reduction of cobalt oxides with hydrogen occurs simultaneously with the appearance of metallic cobalt and disordered defective nonstoichiometric cobalt oxides, removal of reaction water from a porous system, oxidation with water of different genesis of already reduced cobalt, and the formation of boehmite from aluminum. Temperature-dependence additionally conditions its subsequent transformations with the production of protospinel and spinel cobalt-containing structures in various ratios.

It is important to note that the temperature of reduction and heat treatment can result in the formation of different dispersion of excess cobalt crystallites relative to the interaction with the corresponding carrier. Such conditions can also lead to the development of distinct crystallographic modifications in the metal cobalt itself. The hcp phase prevails in massive cobalt crystallites at low temperatures (up to 298 K). Up to a temperature of 500°C, it coexists with the face-centered cubic (fcc) phase, which stabilizes at average temperatures of about 200°C, while above 500°C, the hcp phase again becomes dominant [19]. Nevertheless, the structure and crystallographic structure of intermediate CoO oxides are also influenced by deformation stresses in crystallites when cobalt nanoparticles are realized in catalysts. This is dependent on the location of particles on different carriers and production conditions, specifically on their dispersion and surface chemistry [20, 21].

The reduction of catalysts in hydrogen on a number of carriers (on silicon, aluminum, and titanium oxides at 250, 300, and 350°C) [22] showed a significant difference in the realized states of cobalt for different carriers. For example, on silica gel, the CoO phase is observed at temperatures above 190°C. Up to 380°C, 29% of CO remains in the oxide form, while the mixed phase of Co^0 (fcc/hcp) occurs after 310°C: the size of the crystallites of Co^0 (hcp) making up about 15% of the total is about 5 nm; the content of the phase of Co^0 (fcc) is twice as large, and it is dominant. Up to the reduction temperature of 430°C, the sizes of the crystallites do not change and there is no sintering. Moreover, when activated at 250°C, this system has the necessary catalytic properties, allowing a significant reduction in both capital and operating costs, which is especially important for small installations.

From a technological standpoint, achieving the minimum requisite reactor heating temperature is conducive to the reduction process, which also informs the specifications for the material used in its construction. The restoration of the catalytic system represents a critical procedure for the entire FTS, necessitating a comprehensive understanding of the fundamental issues and conditions that are essential for normal operation. From both applied and theoretical standpoints, investigating this problem for a modern industrial FTS catalyst, such as the impregnating catalyst INFRA S2 on a granular carrier with high thermal conductivity containing thermally expanded graphite (TEG) or, synonymously, penografite [23], is a worthwhile endeavor.

The purpose of this study was to determine under laboratory conditions the temperature dependence of the degree of reduction of the FTS catalyst with a highly efficient heat-conducting network due to the percolation effect and to test a catalytic system having a low reduction temperature at a pilot plant.

EXPERIMENTAL

The paper investigates a carrier and a 20% cobalt catalyst (of one batch) S2 based thereupon, which were prepared at *INFRA* (Russia). The starting materials for extrusion and for catalyst preparation were boehmite DISPERAL P2 (produced by *SaSol*, Germany); zeolite Hβ Zeolyst™ CP 814C *(Zeolyst*, USA); thermally expanded graphite TEG-50/4 (*R&D UNIKHIMTEK*, Russia); $Co(NO_3)_2 6H_2O$ (GOST 4228-78[1], analytical or reagent grades without nickel, *SPC 'Baltiyskaya Manufaktura'*, Russia). The corresponding solutions are obtained on the basis of distilled water.

Cylindrical granules of the carrier of the initial mass composition (50% DisperalP2 + 30% zeolite Hß with a modulus of 38 + 20% TEG) and a size of 1.5 × (2–4) mm were obtained by extrusion, then impregnated with a solution of cobalt nitrate and calcined in accordance with the existing regulations at the *INFRA* catalytic factory. In order to ascertain the correct data for determining the degree of reduction (without the confounding effect of diffusion factors), the granules were subjected to mechanical grinding in an agate mortar. The resulting powder fraction was 0.2–0.4 mm. A single sample of the powder subsequently used in all subsequent experiments was thermally vacuumed (350°C, 3 h, 10^{-3} mmHg) in a cuvette on an Autosorb-1C device (*Quantachrome Instruments*, USA). The initial powdered catalyst S2 lost 9.67% of its mass, which corresponds to a cobalt content of ~17 wt % in the studied sample. This value converges with the spectrophotometrically determined concentration of 20% cobalt in a freshly calcined carrier, with a calculated cobalt content of 18 wt %. The aforementioned figures are elucidated as follows: 100 g of the calculated catalyst, containing 20% cobalt (by preparation), comprises 80 g of dry carrier and 20 g of Co metal. Following decomposition of nitrate to Co_3O_4, these dry calculated 100 g should actually weigh 107.24 g (considering the weight of cobalt oxide 27.24 g instead of 20 g of Co^0). The actual wet catalyst has lost 9.67% of its mass, i.e., every 100 g of the studied sample contains 90.33 g of an idealized dry catalyst with cobalt in the oxide form of Co_3O_4. A total of 16.85 g of metallic cobalt is present in the 90.33 g of the substance under examination. This figure is based on the proportion of 20 g of cobalt per 107.24 g of the dry catalyst used for preparation. However, the weight of the sample with 16.85 g of cobalt was initially 100 g; therefore, the concentration of metallic cobalt in the initial catalyst under study was 16.85%. Thus, the actual concentration of cobalt in the granules loaded into the reactor is 17–18 wt %.

The catalyst powder was activated directly in the U-shaped flow cell of the device under the conditions of the catalytic experiment (i.e., 300–400°C and appropriate time). The restoration was carried out with hydrogen grade B 6.0 (analytical grade, TU 2118-06-18136415-06, *Moscow Gas Processing Plant*, Russia) followed by partial blow-off in helium grade "A" (TU 0271-135-31323949-2005, *Moscow Gas Processing Plant*, Russia) from sorbed reaction water and residual hydrogen. After initial reduction, the sample in the cuvette was cooled to 40°C during vacuuming. In the same cell, without contact with air, the catalyst was restored at a volume flow rate of dry hydrogen $(30–60) \cdot 10^3$ h^{-1} to a temperature of 980°C on Autosorb-1C with fixation of thermoprogrammed reduction curves after preliminary reduction (TPR-PR) at a given activation temperature.

It should be noted that, in contrast to a granular catalyst in a reactor, the maximum possible reduction level is achievable under these conditions, which are not complicated by diffusion.

In order to accurately quantify the consumption of hydrogen, the katharometer signal was recorded for the drained gas stream that passed through a low-temperature (−95 to −80°C) regenerated zeolite trap following the reaction. The weight of the samples was recorded before and after the experiment. The experimental TPR-PR data were processed in the Origin Pro8 program[2] with baseline subtraction. The degree of reduction was quantified by measuring the ratio of the total effect areas in the range of 50–980°C from the S2 catalyst (which exhibited complete reduction) and that following preliminary reduction in the specified modes.

An STA 449 F1 complex thermal analysis device (*Netzsch*, Germany) was also used to study the systems.

The catalyst activated at a temperature of 325°C for 6 h with a volumetric flow rate of 3000 h^{-1} of hydrogen in a 0.5-inch reactor (12 cm^3 of granular catalyst S2, bulk density 0.658 g/cm^3) was tested in an experimental installation according to the previously described method [24]. The data obtained during testing were compared with the results in the standard activation mode (400°C, 3000 h^{-1} H_2, 1 h). The composition of synthesis gas and gaseous, as well that of liquid products, was analyzed on a Crystal-Lux 4000M chromatograph (*Meta-Chrome*, Russia).

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[2] https://www.originlab.com/. Accessed December 23, 2024.

RESULTS AND DISCUSSION

Figure 1 presents a summary of the data pertaining to the degrees of reduction of catalysts at varying temperatures and pretreatment times.

The control of reproducibility of the results for a number of experimental points with different sample weights (the initial sample of the S2 catalyst with a zero degree of reduction and restored for 1 h at 350 and 400°C), as well as when processing TPR-PR curves with a change in the zero-line parameters, showed that the discrepancy from the average was no more than 5%.

For the described method, the potential for minor discrepancies in the measured values of the degree of reduction as a result of the consumption of hydrogen when interacting with the free surface of thermally expanded graphite in the catalyst composition is not a significant concern due to the comparison of identical samples following duplicate processing. While the diffusion of metal over the surface with different treatments may result in slight alterations to the absolute figures, it does not impact the reduction dynamics, which are contingent upon the experimental conditions. The diffusion of metal over the surface with different treatments may result in slight alterations to the absolute figures, but does not impact the dynamics of the degree of reduction, which is contingent upon the experimental conditions. At the same time, the intensity of the TPR signal of the initial S2 carrier after 10 h of thermal vacuum treatment at 300°C is significantly less than after 3 h. This suggests the presence of a substantial number of recoverable surface centers, which necessitates the comparison of samples with strictly identical characteristics to offset the impact of the catalyst surface.

As follows from the thermogravimetric data, catalysts in the helium flow for the range 700–900°C have sharp mass losses that are not typical for carrier components (including TEG). In the case of catalyst granules having a diameter of 1.5 mm in the temperature range of 723–862°C, these losses are about 9.2 wt %, and for granules with a diameter of 2.5 mm in the temperature range of 800–885°C—about 8.1 wt %. If we assume that all of losses are due to the formation of CO or CO_2 during thermolysis due to the autothermal reduction of cobalt oxides with carbon [25], then, counting on the transformations of Co_3O_4 (also for Co_2O_3), this gives a complete conversion of metal oxides to Co^0 when CO_2 occurs. Thus, almost all of the deposited oxidized cobalt is reduced by carbon in this temperature range. This means that in the initial catalyst, the oxidized metal (including in the form of embedding structures and protospinel formations) is located on the surface of the TEG in the form of polylayers fixed to this component of the carrier or in sufficient proximity to it, which allows for the possibility of high-temperature diffusion-thermal interaction with carbon to determine the efficiency of heat removal in the FTS. Accordingly, at low temperatures, due to strong interaction with the carrier, their reduction is difficult. Nevertheless, the quantitative loss of the degree of reduction can be partially compensated for the catalyst in FTS by the increased activity of highly dispersed cobalt located on the oxidized metal. According to the data of [17, 25], cobalt oxide crystallites on the carbon surface (TEG, nanotubes) are characterized by a particle size less than 20 nm that is close to optimal in FTS in terms of selectivity with C_{5+}. At the same time, the amount of cobalt in direct contact with carbon recorded by the mapping method of energy dispersive X-ray spectroscopy and a scanning electron microscope in [17] is small, being (as found for the model catalyst only on TEG) mainly located at the ends of carbon plates.

The degree of reduction varies slightly after 1 h of treatment in the range of 300–350°C and increases only at 380–400°C (Figs. 1 and 2). At the same time, the number of disordered spinel and protospinel cobalt-containing phases fixed on the surface in the temperature range 500–800°C [18] varies slightly. When reduced at temperatures up to 350°C, low-temperature peaks from surface hydrated structures are almost constant; however, when reduced at 380°C, due to better dehydration of the surface, a solid solution of CoO in Co_3O_4 is formed, which is fixed by the maximum TPR-PR characteristic of large particles of cobalt oxides of about 400°C.

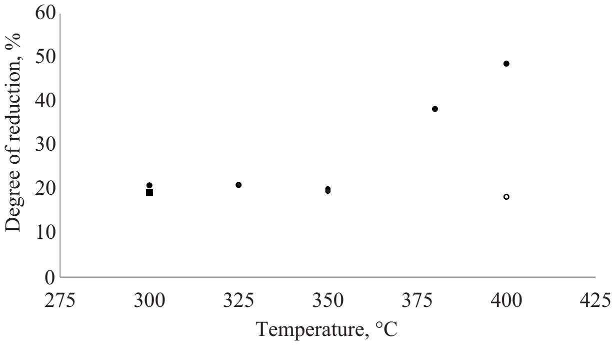

Fig. 1. Degree of reduction of S2 catalyst (fraction of 0.2–0.4 mm) at different temperatures and reduction times. The samples were pre-annealed in vacuum at 350°C for 1 h, then reduced during 1 h (black and white circles) or 4 h (square). A white-circle sample was additionally pre-heated at 400°C in He flow for 5 h

As follows from the analysis of Figs. 1 and 3, an increase in reduction time at low temperature (300°C) does not affect the degree of reduction (black circles and square, Fig. 1); however, pretreatment for 5 h in an inert gas flow at 400°C more than halves (white circle, Fig. 1) the degree of reduction. The latter is attributable to the intensification of interaction with the carrier and the emergence of spinel-type cobalt-containing structures that are irremediable under these conditions (see Figs. 3 and 4).

At the same time, the maximum value of the reduction of residual phases from Co_3O_4 to CoO also decreases (the first maximum) with increasing temperature (Fig. 2). However, as can be seen from Figs. 3 and 4, its relative intensity increases in the case of prolonged reduction or thermolysis. This indicates their active formation due to surface diffusion both during thermolysis and reduction, as well as subsequent oxidation due to functional surface groups of cobalt-containing structures. It is evident that the reduction in the observed degree of reduction resulting from the use of non-dried hydrogen in a humid environment will be relative.

The table compares the results of catalytic testing of the S2 catalyst (synthesis gas $H_2 : CO = 2 : 1$) recovered under selected activation conditions (325°C, 3000 h^{-1} H_2, 6 h) in a single-section tube reactor of *INFRA* of the pipe-in-pipe type with the results for standard conditions (400°C, 3000 h^{-1} H_2, 1 h) having an equal bulk density of the catalyst (0.66 g/cm^3).

The data were obtained under stationary conditions following a gradual increase in temperature and synthesis gas consumption. The necessity for the development of a catalyst to prevent overheating arises from the fact that this phenomenon is associated with deactivation as a result of the agglomeration of cobalt particles and increased interaction with the carrier.

As can be seen from the table, the most significant differences are observed in the selectivity of the formation of C_{5+} hydrocarbons, which is maximal with low-temperature reduction of absolutely identical initial catalysts with the same gas and hydrodynamics in the reactor.

This is in good agreement with the increase found for the S2 catalyst at a low reduction temperature or during prolonged thermolysis of the content of oxidized cobalt states (steinerite phases) due to interaction with surface hydroxyls. The same processes are observed in systems comprising a heat-conducting network of metallic aluminum, as well as in catalysts lacking a heat-conducting component on carriers of diverse natures. It is obvious that during the primary low-temperature reduction, a large number of $Co^{\delta+}$ structures are realized on which C_{5+} hydrocarbons are selectively formed [26].

When considering the dynamics of temperature influence and the magnitude of initial reduction on catalytic parameters, it is important to note that the relevant figures obtained are only determined for these systems following a period of 6–7 days

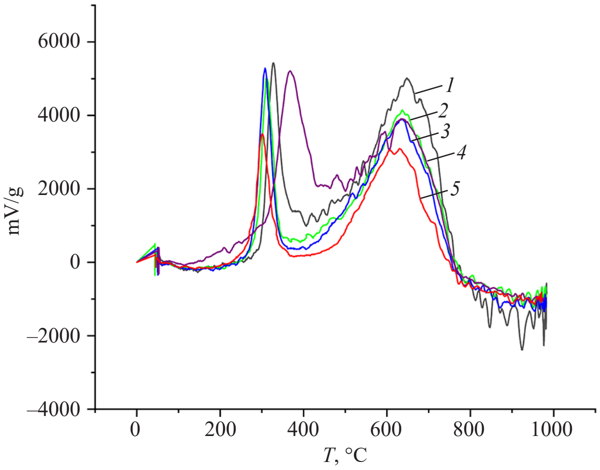

Fig. 2. Curves of thermoprogrammed reduction (TPR) after reduction of S2 catalyst for 1 h at different temperatures, °C: *1* — 300; *2* — 325; *3* — 350; *4* — 380; *5* — 400

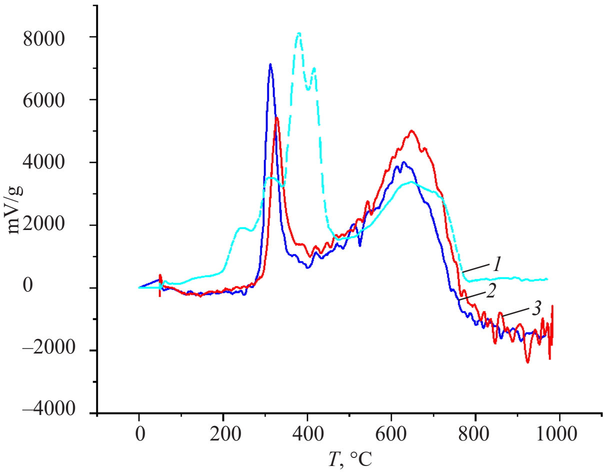

Fig. 3. TPR curves of the initial S2 catalyst (*1*) and after preliminary reduction of the catalyst at 300°C for 4 h (*2*) and 300°C for 1 h (*3*)

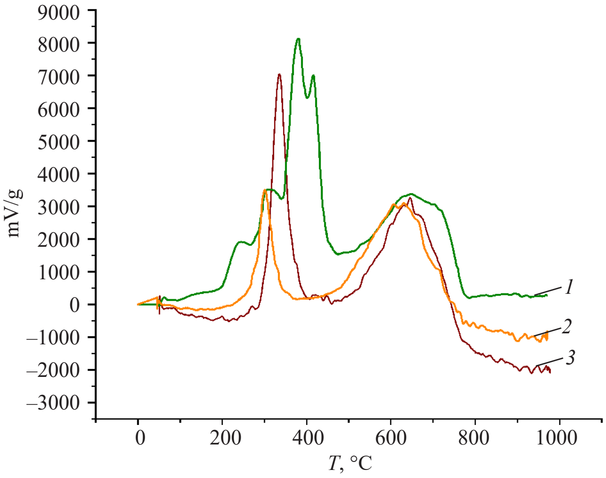

Fig. 4. TPR curves of the initial S2 catalyst (*1*) and after preliminary thermolysis of the catalyst at 400°C for 5 h with reduction at 400°C for 1 h (*2*) or without thermolysis (*3*)

Table. Comparison of catalytic performance of catalysts reduced at different temperatures

Activation conditions	*T*, °C	Gas hourly space velocity, h^{-1}	CO conversion, %	Selectivity of C_{5+} formation, %	Productivity, C_{5+}, g/(L·h)
325°C, 3000 h^{-1} H_2, 6 h	242	3000	56.4	63.7	207.4
400°C, 3000 h^{-1} H_2, 2 h	243		53.9	54.9	173.3

of catalyst development. This can be accompanied by additional activation of the systems (when restored in synthesis gas, an acceptable conversion is achieved after a week of development [8]), as well as their deactivation.

Thus, a catalyst with a higher initial degree of reduction and sufficiently large cobalt agglomerates is partially deactivated during the FTS due to the deposition of synthesized high-molecular hydrocarbons and metal coalescence with the formation of even larger aggregates with lower activity. For small crystallites formed in the S2 catalyst at a low reduction temperature, there is less mobility due to the bond with the surface and better activity both due to the realized structure and due to their large number (Figs. 3 and 4). At the same time, for unambiguous conclusions, it is necessary to determine the actual degrees of reduction of systems following prolonged operation and the extraction of catalysts from the reactor.

CONCLUSIONS

Zeolite-containing cobalt catalysts for FTS with a highly efficient heat-conducting network based on graphite of the TRG brand were studied by the TPR method after preliminary reduction with hydrogen at 300–400°C. It is shown that the catalysts reduced at low temperatures (325°C), despite the low degree of reduction, have the best catalytic parameters. This was demonstrated during the operation of the *INFRA* experimental installation of FTS.

The improvement of the catalytic parameters of the systems is caused by the more efficient implementation of highly dispersed cobalt-oxide structures fixed on the hydrated surface, which cause the appearance of $Co^{\delta+}$ centers with increased activity and selectivity of the formation of C_{5+} hydrocarbons during the reaction.

The obtained data open up the possibility for optimizing technology for reducing FTS catalysts using lower temperatures and with reduced requirements for the thermal stability of the materials used.

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Authors' contribution

All authors equally contributed to the research work.

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