

Effect of Re and Al₂O₃ Promotion on the Working Stability of Cobalt Catalysts for the Fischer–Tropsch Synthesis

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Abstract—The results of the working stability studies of cobalt catalysts based on SiO₂ and Al₂O₃ promoted with Re and Al₂O₃ in the synthesis of hydrocarbons from CO and H₂ in continuous tests for 200–300 h are presented. The prepared catalysts were characterized by transmission electron spectroscopy, temperature-programmed reduction with hydrogen, temperature-programmed desorption of CO, and X-ray fluorescence spectroscopy and tested at a temperature 200°C, a pressure of 0.1 MPa, and a GHSV of 100 h⁻¹. It was determined that a cobalt–silica catalyst promoted with Al₂O₃ had the highest activity. It was established that the addition of Al₂O₃ to a cobalt–silica catalyst increased the conversion of CO and selectivity for C₅₊ hydrocarbons and inhibited the agglomeration of Co particles under the action of a reaction atmosphere in the Fischer–Tropsch synthesis. It was found that the initial conversion of CO increased by a factor of 2 upon the introduction of 0.1 wt % rhenium into the Co/γ-Al₂O₃ catalyst; however, the rate of its deactivation increased in this case due to an almost twofold increase in the size of cobalt particles in the course of synthesis after operation for 300 h.

Keywords: Fischer–Tropsch synthesis, cobalt catalyst, working stability, C₅₊ hydrocarbons

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INTRODUCTION

The development of technologies for the production of synthetic hydrocarbons based on the Fischer–Tropsch (FT) synthesis is of considerable current interest primarily due to the need of converting non-traditional carbon-containing resources (associated petroleum gas, coal, biomass, etc.) and more stringent requirements imposed on the products obtained [1–3]. The FT synthesis is a heterogeneous catalytic process, which allows one to obtain a wide range of hydrocarbon products from CO and H₂ depending on the catalyst used and synthesis conditions [4, 5]. Supported cobalt catalysts based on Al₂O₃, SiO₂, and TiO₂ are most widely used in industry [6–8]. With the use of supports based on Al₂O₃ and TiO₂, a portion of cobalt forms difficult-to-reduce compounds with the support, which are inactive in the FT synthesis [9, 10]. It is possible to decrease the degree of metal–support interactions and increase selectivity for the formation of target products by the introduction of promoters—the noble metals Pt, Re, and Ru [16–18].

Abbreviations: FT, Fischer–Tropsch synthesis; TEM, transmission electron microscopy; TPR-H₂, temperature-programmed reduction with hydrogen, TPD, temperature-programmed desorption; XRF, X-ray fluorescence analysis; and GHSV, gas hourly space velocity.

The stable operation of catalysts in a continuous mode is important for the industrial use of catalysts in order to produce C₅₊ hydrocarbons. Recently, a technology was developed and a pilot batch of cobalt–silica gel catalysts promoted with alumina was manufactured at ZAO Samara Catalyst Plant [19]. It was of interest to determine the stability of this catalyst and compare it with that of well-known samples.

Therefore, the aim of this work was to study the working stability of cobalt catalysts on various supports in the synthesis of hydrocarbons from CO and H₂ in continuous long-term tests.

EXPERIMENTAL

Preparation of Hydrocarbon Synthesis Catalysts

The following four FT synthesis catalysts were prepared: Co/SiO₂, Co–Al₂O₃/SiO₂, Co/γ-Al₂O₃, and Co–Re/γ-Al₂O₃.

The catalysts were prepared by the impregnation of porous supports. KSKG silica gel from OOO Salavat Catalyst Plant (GOST [State Standard] 3956-76) and AN γ-Al₂O₃ from OOO Novomichurinsk Catalyst Plant (TU [Technical Specifications] 2163-142-60201897-2010) were used as the supports.

An impregnation solution of cobalt nitrate (Co(NO₃)₂) with a concentration of 55% was used to prepare the catalysts. The support granules were immersed in the impregnation solution of cobalt nitrate and kept for 0.5 h at a temperature of 70–80°C. Rhenium was introduced into the catalysts by coimpregnation with cobalt nitrate and ammonium perchlorate (NH₄ReO₄). The concentration of ammonium perchlorate in the impregnation solution was maintained in such a way that the Re content of the prepared catalyst was 0.1 wt %. The procedure used for preparing the Co–Al₂O₃/SiO₂ catalyst included the joint impregnation of the support with cobalt and aluminum nitrates [19].

After impregnation, an excess of the impregnation solution was removed, and the wet catalyst granules were subjected to heat treatment under the temperature-programmed conditions: 80°C, 4 h; 100°C, 1 h; 120°C, 1 h; 140°C, 1 h; and 400°C, 4 h; the heating rate was 10 K/min.

Catalyst Characterization Procedures

The cobalt content of the catalyst samples was determined by X-ray fluorescence analysis (XRF) on an ARLQUANT'X spectrometer (Thermo Scientific, Switzerland) under the following conditions: an atmosphere of air, a Teflon substrate, and an effective irradiation area of 48.9 mm².

The freshly prepared catalysts were studied by temperature-programmed reduction with H₂ (TPR-H₂) using a ChemiSorb 2750 analyzer (Micromeritics, the United States) with a thermal conductivity detector (TCD). A sample of 0.1–0.15 g was placed in a quartz reactor arranged in a temperature-programmed furnace. Before the onset of TPR-H₂, the catalyst sample was kept in a flow of He (20 mL/min) for 2 h at a temperature of 200°C to remove moisture and other adsorbed gases. Then, the sample was cooled to room temperature and the flow was switched to a mixture of 10% H₂ and 90% N₂ (20 mL/min). The reduction process was studied in a temperature range of 20–800°C with a heating rate of 5 K/min.

The catalysts were studied by the temperature-programmed desorption (TPD) of CO using a ChemiSorb 2750 analyzer (Micromeritics, the United States) with a thermal conductivity detector (TCD). A sample of about 0.1 g was placed in a U-shaped quartz reactor and kept in a flow of helium (20 mL/min) for 2 h at a temperature of 200°C to remove moisture and other adsorbed gases. Reduction with a hydrogen–nitrogen mixture (10% H₂ and 90% N₂) was carried out for 1 h at a temperature of 400°C. The pulse adsorption of CO was carried out at 20°C in a flow of helium (20 mL/min) until the surface of the sample was saturated. After saturation, the sample was purged with helium (20 mL/min) for 1 h at a temperature of 100°C to remove physically adsorbed gas. The desorption of

CO was carried out by increasing the temperature from 100 to 800°C at a rate of 20 K/min.

The study of the catalysts by transmission electron microscopy (TEM) was carried out using a Tecnai G² Spirit BioTWIN microscope (FEI, the Netherlands) with an accelerating voltage of 120 kV. A sample of the initial catalyst was preliminarily reduced with a nitrogen–hydrogen mixture (10% H₂ + 90% N₂) by linear heating from room temperature to 500°C for 1 h. The samples were ground in a flow of CO₂ and applied to copper gauze in the form of suspensions (isopropyl alcohol–catalyst).

The particle size distribution of cobalt crystallites in prerduced catalysts was determined using transmission electron microscopy. The average crystallite size was calculated from the following formula [20]:

$$d_{\text{av}}(\text{Co}^0) = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}, \quad (1)$$

where n_i is the number of particles with a diameter d_i .

The dispersity of cobalt (D , %) was calculated based on these data [21]:

$$D = \frac{96}{d_{\text{av}}(\text{Co}^0)}, \quad (2)$$

where $d_{\text{av}}(\text{Co}^0)$ is the average crystallite size of metallic cobalt, nm.

The standard deviation was determined from the formula [30]

$$\sigma = \sqrt{\frac{\sum n_i (d_i - d(\text{Co}^0))^2}{\sum n_i}}. \quad (3)$$

Hydrocarbons were removed from the pores of catalysts after the synthesis (washed out) in a Soxhlet extractor. For this purpose, a Schott filter with a catalyst sample was placed in a reservoir located at the center of the extractor. 1,2-Dimethylbenzene (*o*-xylene) and *n*-heptane were used as solvents. The catalyst washing procedure included the extraction of hydrocarbons with *o*-xylene (2 h at a temperature of 144°C) and then extraction with *n*-heptane for 1 h at a temperature of 98°C.

The Fischer–Tropsch synthesis of hydrocarbons was carried out in a steel flow reactor ($d_{\text{in}} = 16$ mm) with a fixed catalyst bed (10 cm³) at atmospheric pressure (0.1 MPa), a GHSV of 100 h⁻¹, and a constant temperature (T) of 200°C. The catalyst samples were preliminarily reduced in a flow of H₂ at GHSV = 3000 h⁻¹ and $T = 400^\circ\text{C}$ for 1 h. The catalysts were activated with synthesis gas by a stepwise increase in the temperature (2.5 K/h) from 150 to 200°C. After the catalyst activation, the synthesis was carried out in a continuous mode for 300 h.

The rate of catalysts deactivation was judged from the parameter R_{CD} (%/h), which shows a decrease in

Table 1. Physicochemical properties of the starting and spent catalysts

Sample	C(Co), %	Starting		Spent	
		* d_{av} , nm	* D , %	* d_{av} , nm	* D , %
Co/SiO ₂	21.9	14.8 ± 2.8	6.5	—	—
Co–Al ₂ O ₃ /SiO ₂	22.8	8.8 ± 1.6	10.9	7.1 ± 2.0	13.5
Co/γ-Al ₂ O ₃	19.9	21.8 ± 5.9	4.4	—	—
Co–Re/γ-Al ₂ O ₃	19.7	13.9 ± 3.6	6.9	27.6 ± 5.2	3.5

* According to TEM data. C(Co), % is the concentration of cobalt in the catalyst; d_{av} , nm is the Co crystallite size; and D , % is the dispersity of cobalt. Dashes indicate that the corresponding values were not determined.

the degree of conversion of CO after catalyst operation for 1 h. R_{CD} was determined using the formula

$$R_{CD} = \frac{X_{CO}^i - X_{CO}^f}{\tau}, \quad (4)$$

where X_{CO}^i is the initial degree of conversion of CO, %; X_{CO}^f is the final degree of conversion of CO, %; and τ is time, h.

The synthesis gas and gaseous synthesis products were analyzed by gas-adsorption chromatography on a Kristall 5000 chromatograph (Khromatek, Russia) with a thermal conductivity detector, a Hayesep R column (Khromatek, Russia), and a column with NaX molecular sieves. The former column was used for the analysis of C₁–C₅ hydrocarbons and CO₂ (carrier gas, helium; flow rate, 15 mL/min), and the latter was used for the analysis of CO, H₂, and N₂ (carrier gas, argon; flow rate, 15 mL/min) under temperature-programming conditions (80–240°C; heating rate, 8 K/min).

RESULTS AND DISCUSSION

Table 1 summarizes the characteristics of the prepared and spent catalysts. These data indicate that the cobalt content of the test catalysts varied in a range of 19.7–22.8%.

Figure 1 shows the TEM images and particle-size distribution diagrams of cobalt crystallites for reduced catalysts.

Cobalt particles 5–20 nm in size occurred on the surface of the Co/SiO₂ catalyst (Fig. 1a); the average particle size was 14.8 nm (Table 1).

The addition of Al₂O₃ to the silica gel catalyst (Fig. 1b) significantly changed the dispersity of the active component: its value increased from 6.5 to 10.9%. The introduction of alumina facilitated a decrease in the cobalt particle size and narrowed the particle-size distribution. It is likely that an additive of 1.0 wt % Al₂O₃ inhibited the aggregation of cobalt metal nanoparticles, which manifested itself in the observed decrease in the average particle size. The distribution became almost unimodal; the average cobalt particle size was 8.8 nm, which is considered optimal for FT synthesis catalysts [22].

The particles of cobalt in the Co/γ-Al₂O₃ catalyst (Fig. 1c) had an average size of 21.8 nm (Table 1). The introduction of rhenium into the composition of Co/γ-Al₂O₃ (Fig. 1d) led to a significant decrease in the average size of cobalt nanoparticles from 21.8 to 13.9 nm (Table 1) and, as a consequence, to an increase in dispersity from 4.4 to 6.9%. The data on the effect of the addition of rhenium to the γ-Al₂O₃-based catalyst are consistent with published results [23–27].

Figure 2 and Table 2 show the TPR-H₂ curves of catalyst samples and their characteristics, respectively.

The TPR-H₂ curves of all of the samples contained two intense reduction peaks (Fig. 2) due to the Co³⁺ → Co²⁺ and Co²⁺ → Co⁰ transitions in ranges of 262–324 and 337–583°C, respectively. A shift of peaks 1 and 2 to a range of higher temperatures was observed for the Co–Al₂O₃/SiO₂ catalyst. This can be a consequence of interactions between the supported particles of cobalt oxide and Al₂O₃ [28].

The ratio S_2/S_1 between the areas of the two main peaks (Table 2) of SiO₂-based catalysts, which indicates the amount of hydrogen consumed in the Co³⁺ → Co⁰ transition, is 3, which corresponds to a theoretically expected value based on the reaction

Table 2. Characterization of the TPR-H₂ profiles of the catalysts

Catalyst	Peak 1		Peak 2		S_2/S_1
	T , °C	area S_1 , %	T , °C	area S_2 , %	
Co/SiO ₂	262	25.0	337	75.0	3.00
Co–Al ₂ O ₃ /SiO ₂	295	25.0	371	75.0	3.00
Co/γ-Al ₂ O ₃	319	51.1	583	48.9	0.96
Co–Re/γ-Al ₂ O ₃	324	50.4	524	49.6	0.98

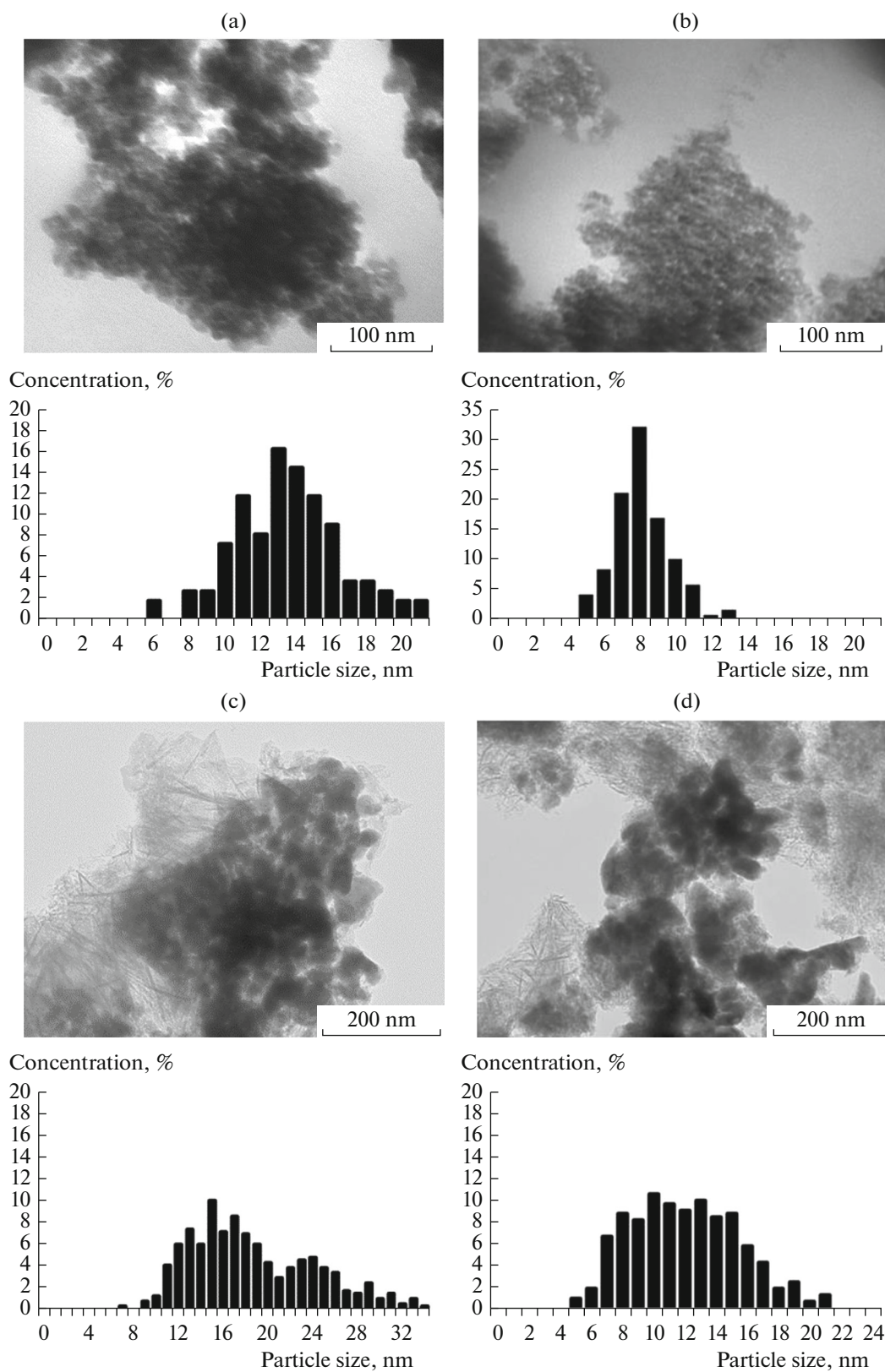


Fig. 1. TEM micrographs of reduced catalysts and bar diagrams of cobalt particle-size distributions: (a) Co/SiO₂, (b) Co-Al₂O₃/SiO₂, (c) Co/ γ -Al₂O₃, and (d) Co-Re/ γ -Al₂O₃.

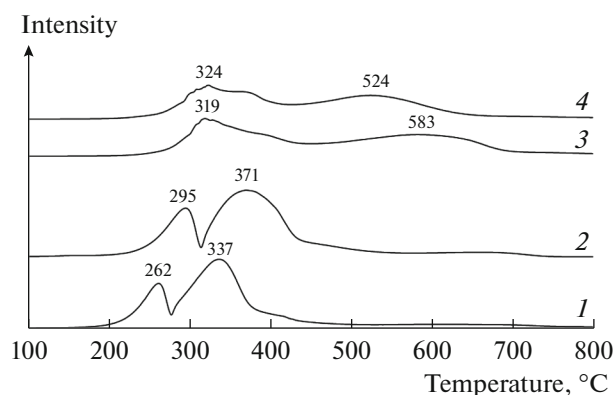


Fig. 2. TPR-H₂ curves of the catalysts: (1) Co/SiO₂, (2) Co-Al₂O₃/SiO₂, (3) Co/γ-Al₂O₃, and (4) Co-Re/γ-Al₂O₃.

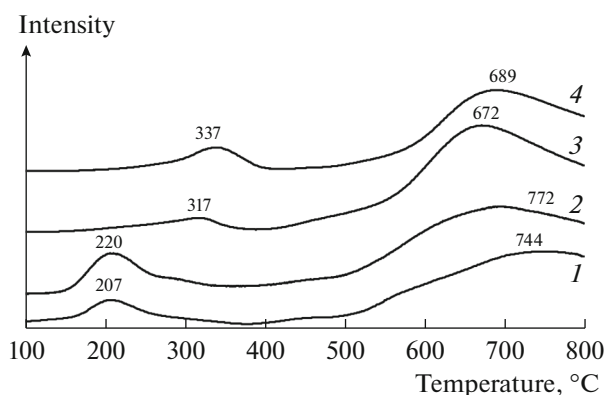


Fig. 3. TPD of CO profiles of the catalysts: (1) Co/SiO₂, (2) Co-Al₂O₃/SiO₂, (3) Co/γ-Al₂O₃, and (4) Co-Re/γ-Al₂O₃.

stoichiometry of the stepwise reduction of cobalt oxide Co₃O₄ to Co⁰ [29].

The addition of rhenium to the Co/γ-Al₂O₃ catalyst led to a shift in the temperature maximum of peak 2 toward a lower temperature without a significant effect on the reduction temperature of cobalt oxide Co₃O₄ to CoO (peak 1). The experimental data on the effect of the rhenium promotion of γ-Al₂O₃-based catalysts on the reduction of CoO to Co⁰ are consistent with the conclusions of Tavasoli et al. [23] on the role of rhenium as a reduction promoter. Smaller S_2/S_1 area ratios for these catalysts may indicate that a portion of cobalt occurred in a difficult-to-reduce form.

The adsorption of CO on reduced catalysts was investigated using the TPD of CO. Figure 3 shows the TPD curves for CO from the reduced samples.

All of the catalyst samples exhibited pronounced profiles of the temperature-programmed desorption of CO. Two major desorption peaks were observed. The first low-temperature peak with a maximum at 207–220°C for catalysts based on SiO₂ or 317–337°C for samples based on γ-Al₂O₃ can be attributed to the desorption of chemisorbed CO. The second high-temperature peak with a maximum at 672–772°C probably appeared as a result of the desorption of CO₂

formed from chemisorbed CO by the Boudoir reaction [30]. The introduction of Al₂O₃ and Re promoters into the catalysts led to a significant increase in the amount of desorbed CO in the temperature range of the appearance of the first peak. Lapidus et al. [31] found that the first peak in the TPD of CO profile corresponds to the weakly bound adsorption of CO in a molecular form on the oxide catalyst surface. It characterizes bifunctional active surface centers involved in the process of polymerization.

Table 3 shows the average values of the main parameters of the catalytic activity of samples in the synthesis of hydrocarbons for 300 h of continuous operation.

All of the test catalysts were active in the synthesis of hydrocarbons from CO and H₂. Under the experimental conditions, Co-Al₂O₃/SiO₂ was most active: the conversion of CO was 78.6%, and selectivity and productivity for C₅₊ hydrocarbons were 64.2% and 11.3 kg m⁻³ h⁻¹, respectively. Promotion with alumina led to a 10.8% increase in the catalyst productivity due to an increase in the conversion of CO and selectivity for C₅₊. In addition, the rate of catalyst deactivation decreased by 9.6% upon the introduction of alumina.

Table 3. Activity of the catalysts in the Fischer–Tropsch synthesis*

Sample	CO conversion, %	Selectivity, %				Productivity of C ₅₊ , kg m ⁻³ h ⁻¹	R_{CD} , %/h
		CH ₄	C ₂ –C ₄	C ₅₊	CO ₂		
Co/SiO ₂	75.3	18.0	15.4	62.8	3.8	10.2	0.052
Co-Al ₂ O ₃ /SiO ₂	78.6	16.5	15.4	64.2	3.9	11.3	0.047
Co/γ-Al ₂ O ₃ **	41.9	14.4	12.1	71.1	2.4	6.4	0.035
Co-Re/γ-Al ₂ O ₃	68.5	17.9	10.7	65.4	6.0	9.5	0.102

* Conditions: 0.1 MPa, 100 h⁻¹, and 200°C.

** The catalyst was tested in a continuous mode for 200 h.

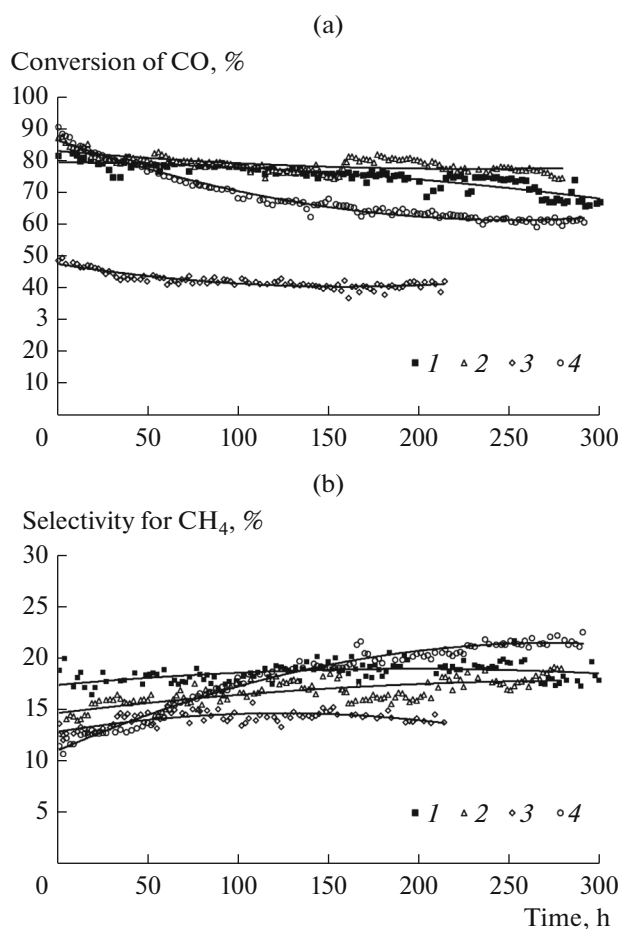


Fig. 4. Dependence of (a) CO conversion and (b) selectivity for CH₄ on the synthesis time: (1) Co/SiO₂, (2) Co–Al₂O₃/SiO₂, (3) Co/ γ -Al₂O₃, and (4) Co–Re/ γ -Al₂O₃.

The introduction of rhenium into the composition of the Co/ γ -Al₂O₃ catalyst increased the degree of conversion from 41.9 to 68.5%. At the same time, the selectivity for C₅₊ hydrocarbons decreased from 71.1 to 65.4% due to the more intense formation of gaseous reaction products C₁–C₄ and CO₂. A significant increase in selectivity for CO₂ (by a factor of 2.5) in the promoted sample may be associated with an increase in the rate of water gas shift reaction due to the facilitation of the dissociative adsorption of CO [32].

The rhenium promotion of the Co/ γ -Al₂O₃ catalyst led to an increase in the rate of its deactivation by a factor of 2.9. Jacobs et al. [33] and Dalai and Davis [34] also noted that the introduction of noble metals into the composition of cobalt catalysts facilitated their accelerated deactivation.

Figure 4 shows the dependence of CO conversion and selectivity for CH₄ on the duration of the synthesis. In general, all of the test catalysts demonstrated a regular decrease in the conversion of CO with time [35]. A decrease in activity was accompanied by a

decrease in selectivity for C₅₊ hydrocarbons due to increased formation of methane and CO₂.

An increase in selectivity for methane with time can be due to the accumulation of liquid C₅₊ hydrocarbons in the pores of the catalyst, which may lead to a decrease in the number of available active chain growth centers [32]. On the other hand, as noted by Iglesia et al. [36], the accumulation of synthesis products in the pores of the catalyst facilitated an increase in the molar ratio H₂/CO inside a catalyst granule due to the different diffusion rates of the reactants. Indeed, Khasin [37] found that the diffusion coefficients of hydrogen and CO through a film of *n*-tetradecane at 200°C are 1.6×10^{-4} and 2.2×10^{-4} m²/s, respectively. This leads to an increase in the ratio H₂/CO on the catalyst surface and an increase in selectivity for methane formation [38].

The first 50 h of synthesis were characterized by the highest rate of decrease in the activity of all of the samples. It is likely that the active component of the catalyst was stabilized during this period under the influence of a reaction atmosphere.

The Co/SiO₂ and Co–Al₂O₃/SiO₂ catalysts exhibited similar initial conversions of CO and selectivity for the formation of C₅₊ hydrocarbons and CH₄. However, after ~250 h of synthesis, a sharp decrease in activity was observed in the Co/SiO₂ sample, which was accompanied by an increase in the fraction of methane formed and a decrease in the productivity of C₅₊ hydrocarbons.

A sharp increase in the degree of CO conversion from 48 to 90% was observed in the initial period upon the addition of rhenium to the γ -Al₂O₃-based catalysts (Fig. 4a). Vada et al. [39] found a similar effect and observed a rapid decrease in the activity of the Co–Re/ γ -Al₂O₃ catalyst in comparison with that of a sample without rhenium.

The loss of catalyst activity is usually caused by a combination of factors that have different effects on the behavior of the catalytic system in the course of synthesis. The formation of a large amount of water at a high degree of CO conversion is considered a main reason for the deactivation of cobalt catalysts based on oxide supports. The effect of active metal oxidation under the action of H₂O leads to a decrease in the metal surface area of a cobalt catalyst [11]. In this case, the rate of oxidation of the active phase is directly proportional to the partial pressure of water [40].

For the TEM study of the catalysts after the synthesis, they were unloaded in a flow of nitrogen and subjected to two-stage washing with *o*-xylene and *n*-heptane in order to remove hydrocarbons from the pores. The TEM data (Fig. 5a, Table 1) showed that the dispersity and particle-size distribution of Co in the Co–Al₂O₃/SiO₂ sample that worked for ~300 h were comparable with those of the initial reduced catalyst (Fig. 1b). It is likely that, in addition to an increase in

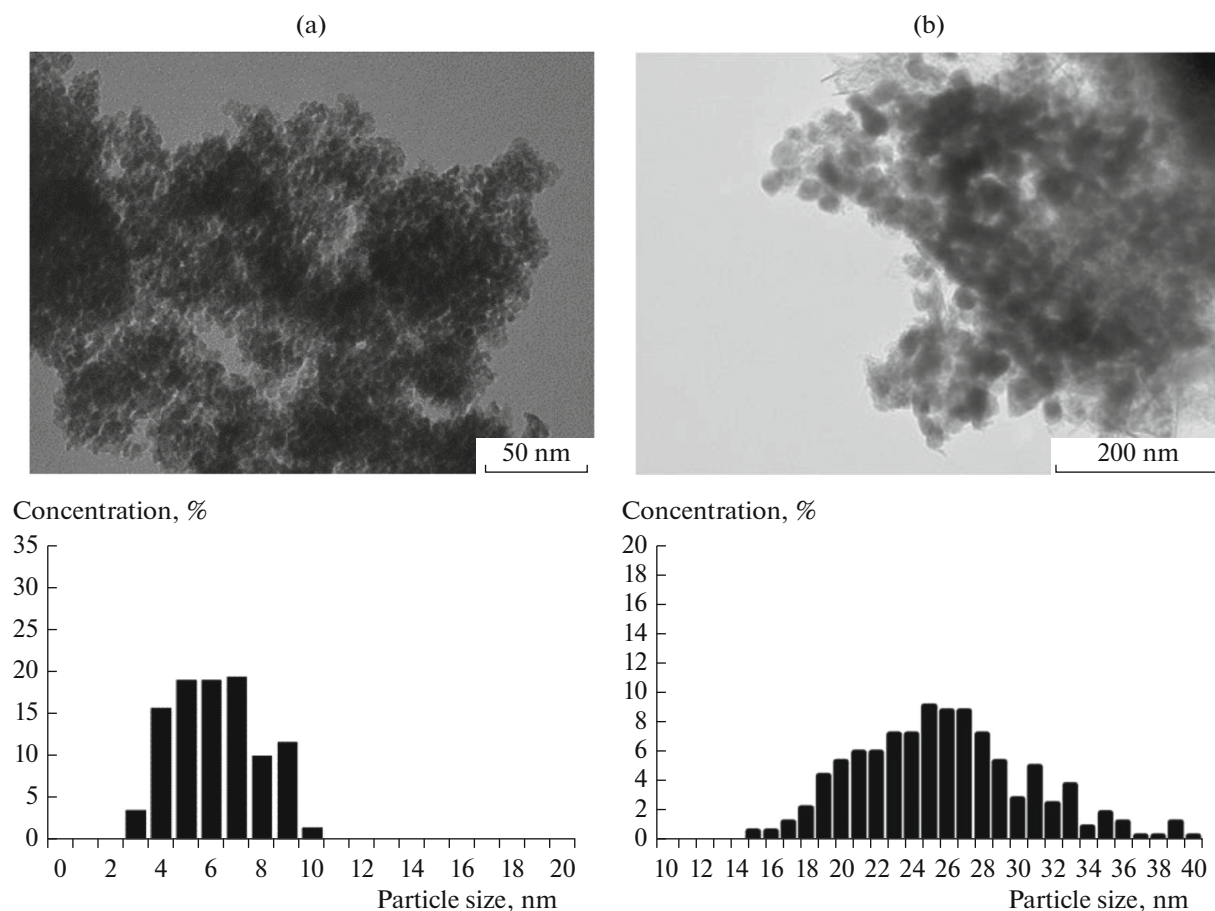


Fig. 5. TEM micrographs of the catalysts after synthesis and bar diagrams of cobalt particle-size distributions: (a) Co–Al₂O₃/SiO₂ and (b) Co–Re/γ-Al₂O₃.

the conversion of CO and the process selectivity for C₅₊ hydrocarbons, the introduction of Al₂O₃ into a cobalt–silica gel catalyst inhibited the aggregation of Co nanoparticles under the action of a reaction atmosphere in the FT synthesis conditions to facilitate stable catalyst operation.

The Co–Re/γ-Al₂O₃ catalyst after 300 h of operation exhibited a significant increase in the average particle size of Co (from 13.9 to 27.6 nm), which was a consequence of the agglomeration of cobalt particles under the action of a reaction atmosphere.

CONCLUSIONS

We studied the working stability of the supported cobalt catalysts in the synthesis of hydrocarbons from CO and H₂ in continuous tests. It was determined that the cobalt–silica gel catalyst promoted by Al₂O₃ had the highest activity. The introduction of Al₂O₃ into Co/γ-Al₂O₃ increased the degree of CO conversion and selectivity for C₅₊ hydrocarbons and inhibited the aggregation of Co particles in the FT synthesis conditions under the action of a reaction atmosphere.

The addition of rhenium to the Co/γ-Al₂O₃ catalyst led to a significant increase (by a factor of ~2) in the conversion of CO in the initial period of catalyst operation (the first 50 h). However, the rate of deactivation on the promoted sample was almost three times higher, probably, due to a twofold increase in cobalt particle sizes under the action of the reaction atmosphere. Nevertheless, the conversion of CO even after 200 h of synthesis in the presence of Co–Re/γ-Al₂O₃ was higher by a factor of 1.5.

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An increase in selectivity for the formation of methane in the course of synthesis was observed on all of the catalysts. This can be a consequence of the

accumulation of liquid C₅₊ hydrocarbons in the catalyst pores, which leads to an increase in the molar ratio H₂/CO inside a catalyst granule due to different rates of diffusion of the reactants.

As a result of this work, we determined that the rate of catalyst deactivation increased in the order Co/γ-Al₂O₃ < Co–Al₂O₃/SiO₂ < Co/SiO₂ < Co–Re/γ-Al₂O₃.

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