

Anionic composition of precursors of the Co/Al₂O₃ catalysts for the Fischer–Tropsch synthesis

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Cobalt and aluminum hydroxo compounds with the hydrotalcite-type structure containing nitrate, carbonate, and hydroxyl groups are formed due to the deposition by precipitation of cobalt cations from a nitrate solution on δ - and γ -Al₂O₃ under the conditions of urea hydrolysis. The influence of the method of preparation on the anionic composition of the hydroxo compounds (precursors of the Co–Al catalyst) was studied. A correlation between the anionic composition of the precursor compound and the catalytic properties of the catalysts in the Fischer–Tropsch synthesis was established.

Key words: Fischer–Tropsch synthesis, oxide Co–Al catalysts, precursor compound, anionic composition of Co–Al catalyst precursor.

The Fischer–Tropsch synthesis is a promising method for the production of motor fuels, waxes, olefins, alcohols, and solid hydrocarbons from the syngas.^{1–3}

The reactions of the Fischer–Tropsch synthesis occur in the presence of catalysts containing the VIII group metals.⁴ The Co-containing catalysts are most frequently used for the hydrogen-enriched syngas obtained by the processing of natural and casing-head gases. The active state of the catalyst is related to the formation of stable dispersed particles of metallic cobalt.

It is known^{5–7} that the catalytic activity and selectivity to hydrocarbons (C₅₊) depend on the composition and structure of the catalyst precursor and methods of its preparation and activation. The introduction of metal promoters,^{8–15} including Platinum Group noble metals,^{16–19} into the composition of the catalyst precursors affects the catalytic properties of the samples. Such oxides as SiO₂, Al₂O₃, TiO₂, and MgO and active carbon are used as supports for the Co-containing catalysts.^{20–26} The modification of the support surface with zirconium and lanthanum additives^{27–29} and alkaline-earth metals Ca, Sr, and Ba (see Ref. 30) improves the catalytic properties of the cobalt-containing systems.

To prepare the Co-containing catalysts, cobalt nitrates, chlorides, sulfates, acetates, and oxalates, as well as cobalt chelates, were used as the starting salts, although the samples prepared from nitrate solutions are more productive

in the Fischer–Tropsch synthesis.^{1,5} The catalyst obtained from cobalt nitrate has a higher conversion of CO and selectivity for C₈₊ than the samples prepared from cobalt acetate and chloride.³¹ When the solutions of Co^{II} nitrate, oxalate, and acetylacetonate and cobalt chelates are used as the starting salts, highly dispersed Co⁰ particles are formed, which determine the high activity of the catalysts.³² Solutions of cobalt nitrates and acetates used for the preparation of the supported cobalt/SiO₂ catalysts exert different effects on the dispersion and reductibility of the metallic cobalt particles that formed.^{33,34} The Co/SiO₂ catalysts prepared by impregnating a support with a mixture of solutions of Co²⁺ nitrate and acetate contain metallic cobalt particles with a higher dispersion than in the catalysts prepared by the impregnation with a nitrate solution or a solution of cobalt acetate only.³⁵ The deposition by precipitation of cobalt cations on γ -Al₂O₃ gives hydroxo compounds with the hydrotalcite-type structure, which are precursors of the catalysts active in the Fischer–Tropsch synthesis.^{36,37}

It was found that the activity of the cobalt catalysts supported on SiO₂ and Al₂O₃, as well as the Ni/SiO₂ catalysts, increased when the precursor compounds are thermally treated in an inert gas flow containing nitrogen oxide.^{38–40} It was assumed³⁹ that the thermal treatment in the presence of nitrogen oxide changed the composition of the oxide precursor of the Ni/SiO₂ catalysts, which

increases the dispersity of metallic cobalt during the activation of the Ni/SiO₂ catalyst.

The influence of the anionic composition of the starting cobalt salts on the formation of active states of the catalysts, in particular, on the dispersion of metallic cobalt particles formed due to the thermal treatment and activation by hydrogen, was studied in rather detail. At the same time, the anionic composition and structure of the precursor compounds and the character of their influence on the catalytic properties remain insufficiently studied.

In the present work, we studied the influence of the anionic composition and structure of the precursor compounds and the conditions of their preparation on the catalytic properties on the Co/Al₂O₃ catalysts of the Fischer–Tropsch synthesis.

Experimental

The catalysts were prepared by the thermal treatment in an inert gas flow of the precursor compounds, alumina and aluminocobalt hydroxo compounds. The latter were obtained as follows: (1) deposition by precipitation of cobalt cations on alumina under the conditions of urea hydrolysis; (2) deposition by precipitation of cobalt cations on alumina with a soda solution and (2') coprecipitation of cobalt and aluminum cation with a soda solution; and (3) impregnation of alumina with a solution of cobalt nitrate.

Solutions of cobalt nitrate (salt reagent cobalt(II) nitrate hexahydrate, pure grade) and aluminum oxide of the modification γ -Al₂O₃ or δ -Al₂O₃ were used. The latter were prepared by the thermal treatment of aluminum hydroxide (JSC "Angarsk Catalysts and Organic Synthesis Plant", trade mark A-64) in air for 2 h at 700 and 910 °C, respectively. The structures of the oxides were confirmed by X-ray diffraction analysis. The specific surface of the supports determined by the BET method was 165 and 127 m² g⁻¹ for γ - and δ -Al₂O₃, respectively. The supports with a granule size of 0.25–0.50 mm and 2.7 × 5.0 mm were used for the preparation of the catalysts.

1. Deposition by precipitation of cobalt cations under the conditions of urea hydrolysis from nitrate solutions of cobalt on γ - or δ -Al₂O₃ (deposition by precipitation with urea)^{41,42} was carried out as follows. The necessary amounts of alumina and urea were added to a solution of cobalt nitrate with stirring, and the mixture was heated to 90 °C and stored under these conditions at a constant volume of the suspension for 7 or 23 h. We used 0.047–3.4 M solutions of cobalt nitrate and 0.047–6.9 M solutions of urea. The initial pH value of the suspension during the preparation of all samples was 6.5–6.6, except sample 10, to the suspension of which a solution of nitric acid was added to pH = 3. At the end of the synthesis the pH of the suspension was 6.6–6.7. After the completion of the synthesis, the precipitate was separated from the mother liquor, washed with distilled water, and dried for 10–15 h under an IR lamp at $T \sim 50$ °C.

2. Deposition by precipitation of cobalt cations with a solution of Na₂CO₃ was carried out from nitrate solutions on δ -Al₂O₃ (the granule size of the support was 0.25–0.50 mm) or (2') by the coprecipitation of 10% solutions of nitrate salts of cobalt and aluminum. The samples were precipitated at pH = 7.3 ± 0.2 and at 65–70 °C. The obtained precipitates were washed

off with distilled water from sodium until its content was ≤ 0.01 wt.%.

3. Deposition of cobalt cations by the impregnation of the γ - and δ -Al₂O₃ supports to incipient wetness with solutions of cobalt nitrate was carried out at room temperature.

The cationic composition of the samples was determined by atomic emission spectroscopy (AES) on an Optima 4300 DV instrument.

Thermal analysis was carried out on a Netzsch STA-449 thermograph in an argon flow (150 mL min⁻¹) at a heating rate of 10 K min⁻¹. Gases evolved were analyzed with a Stanford Research System UGA-200 mass spectrometer. The content of the NO₃⁻ anion was estimated by the signal of the mass spectrometer at 30 amu (NO), the content of the CO₃²⁻ anion was determined by the signal at 44 amu (CO₂), and the amount of evolved water was found by the signal at 18 amu.

X-ray diffraction studies were carried out on Bruker D8 and X'TRA diffractometers (Thermo Electron Corporation, Switzerland) in Cu-K α radiation with a reflected-beam monochromator.

Catalytic properties of the catalysts in reactions of CO hydrogenation were determined at 210 °C and pressures of 1 and 21 atm.

The samples with the granule size 0.14–0.25 mm (weighed sample 1 g) were studied in a flow isothermal tubular reactor (diameter 3 mm) with the stationary granule bed. The single-row Temkin reactor⁴³ (diameter 4 mm) was used for the study of the samples with the granule size 2.7 × 5.0 mm. If the reaction mixture of the composition CO : H₂ : N₂ = 30 : 60 : 10 (vol.%) was fed at $P = 1$ atm with a flow rate of 2000–4000 h⁻¹, the conversion of CO ranged from 10 to 20%, whereas at $P = 21$ atm and a flow rate of 2000–6000 h⁻¹ it was within 20–25%. The gas mixtures and condensate were analyzed by the chromatographic method with Tsvet-530 and Tsvet-560 chromatographs with flame-ionization detectors and a thermal conductivity detector. A capillary quartz column and a column packed with active carbon was used for the separation of components of the gas mixtures. The components of the condensates were separated on a capillary quartz column with the stationary liquid phase SE-54.

Prior to catalytic tests, the samples were preheated in an argon flow at 250–270 °C and then reduced in a hydrogen flow at 600 °C.

The specific catalytic activity expressed in the rate of CO conversion per time unit referred to the amount of cobalt in the catalyst was taken as a measure of activity of the samples.

Results and Discussion

Influence of the method and conditions of preparation on the composition and structure of the Co–Al hydroxo compounds. The compositions and preparation conditions of samples of the hydroxo compounds (precursors of the catalysts) are given in Table 1. The ratio of the cobalt and aluminum cations was determined in the calcined sample on the basis of the experimental data on elemental analysis (AES) and mass loss conducted by heating the dry sample in argon to 450 °C (thermogravimetric analysis).

Composition of the hydroxo compounds obtained by the impregnation method and deposition by precipitation with

Table 1. Conditions of preparation and the composition of the Co—Al samples

Sample	Support (granule size, d/mm)	Concentration of Co(NO ₃) ₂ in solution /mol L ⁻¹	Ratio Co : (NH ₂) ₂ CO	Ratio Co : Al (atomic fractions)	Duration of synthesis /h
1 ^a	γ-Al ₂ O ₃ (0.25—0.50)	0.074	0.4	0.13	7
2 ^a	The same	0.054	0.4	0.14	23
3 ^a	»»	0.343	0.4	0.21	7
4 ^a	»»	0.075	0.4	0.29	23
5 ^a	»»	0.222	0.5	0.33	23
6 ^a	»»	0.166	0.3	0.38	23
7 ^a	δ-Al ₂ O ₃ (0.25—0.50)	0.054	0.4	0.12	23
8 ^a	The same	0.075	0.4	0.22	23
9 ^a	»»	0.047	1.0	0.14	23
10 ^b	»»	0.047	1.0	0.11	23
11 ^a	»»	0.222	0.5	0.43	23
12 ^a	»»	0.166	0.3	0.38	23
13 ^a	γ-Al ₂ O ₃ (2.7×5.0)	0.343	0.4	0.11	7
14 ^a	δ-Al ₂ O ₃ (2.7×5.0)	0.074	0.4	0.05	7
15 ^a	The same	3.436	0.5	0.17	7
16 ^c	δ-Al ₂ O ₃ (0.25—0.50)	0.593	—	0.53	—
17 ^d	γ-Al ₂ O ₃	0.593	—	1.00	—
18 ^e	δ-Al ₂ O ₃ (0.25—0.50)	1.694	—	0.13	—
19 ^e	γ-Al ₂ O ₃ (0.25—0.50)	4.014	—	0.40	—

^a Deposition by precipitation of cobalt cations on the support with urea.

^b Deposition by precipitation of cobalt cations on the support with urea; in this experiment, pH_{init} = 3.

^c Deposition by precipitation of cobalt cations on the support with a soda solution.

^d Coprecipitation of cobalt and aluminum cations with a soda solution.

^e Deposition of cobalt cations by the impregnation of the support.

a soda solution. The diffraction patterns of the precursor compounds obtained by the impregnation of cobalt cations (*a*) and deposition by precipitation of cobalt cations on alumina with a soda solution (*b*) are presented in Fig. 1. The diffraction pattern analogous to that in Fig. 1, *b* is observed for the sample prepared by the coprecipitation of cobalt and aluminum cations with a soda solution. A comparison of the position and intensity distribution of the diffraction lines of the samples with the reference data shows that the samples obtained by the impregnation method (see Fig. 1, *a*) contain the alumina phase and cobalt crystalline hydrates Co(NO₃)₂·4H₂O [JCPDS PDF 018-0425] and Co(NO₃)₂·6H₂O [JCPDS PDF 012-0572]. As can be seen from the data in Fig. 1, *b*, the samples obtained using the deposition by precipitation of cobalt cations with a soda solution and the coprecipitation of the components contain two phase in addition to alumina: cobalt hydroxocarbonate and cobalt—aluminum hydroxo compounds with the structure of the hydrotalcite type [ICDD PDF 41-1428].

The thermal curves and mass spectra of gases evolved upon the calcination of the sample obtained by the impregnation of γ-Al₂O₃ with a cobalt nitrate solution (the samples with the ratio Co : Al = 0.40 atomic fractions) are shown in Fig. 2. A similar spectrum is observed for the sample with the content Co : Al = 0.13 atomic fractions.

The mass spectrum exhibits a narrow signal in the curve corresponding to a mass of 30 amu, which is referred to

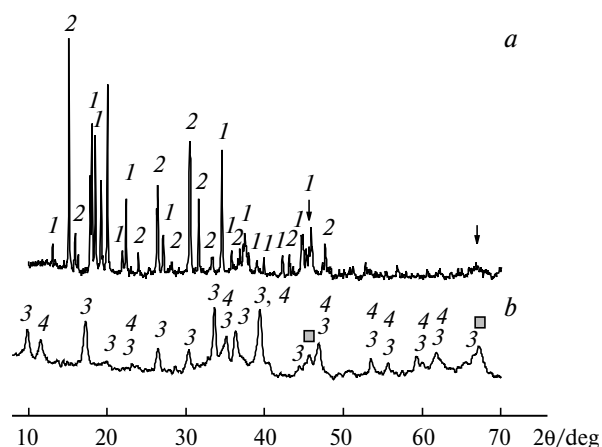


Fig. 1. Diffraction patterns of the precursor compounds obtained using (*a*) the deposition of cobalt cations by impregnation of γ-Al₂O₃, Co : Al = 0.40 atomic fractions: Co(NO₃)₂·4H₂O (1), Co(NO₃)₂·6H₂O (2); (*b*) the deposition by precipitation of cobalt cations with soda on δ-Al₂O₃, Co : Al = 0.53 atomic fractions: Co(CO₃)_{0.5}(OH)·0.11H₂O (3), and the phase with the hydrotalcite type structure, Mg₆Al₂(OH)₁₆CO₃·4H₂O (4). Here and in Fig. 5, arrows correspond to the modification γ-Al₂O₃ [ICDD PDF 10-425] and squares correspond to the modification δ-Al₂O₃ [ICDD PDF 46-1215].

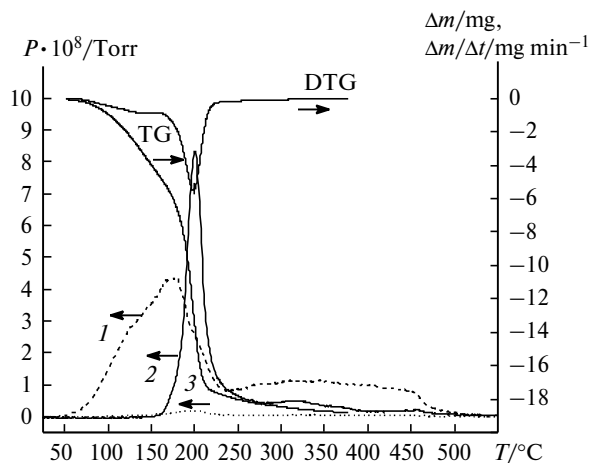


Fig. 2. Thermal curves in argon and the mass spectra of the evolved gas for the sample obtained by the impregnation of γ - Al_2O_3 (granule size 0.25–0.50 mm), Co : Al = 0.40 atomic fractions: MS = 18 (1), 30 (2), and 44 amu (3); P is the pressure of the gas evolved during heating of the hydroxo compounds in an inert gas flow.

the fragments of nitrogen oxides (NO_x), and a broad signal with rather distinct division into two steps in the curve corresponding to a mass of 18 amu. Such a signal is characteristic of water molecules evolved upon desorption and in the process of subsequent dehydroxylation of the hydroxo compound. The spectrum contains almost no signal in the curve attributable to a mass of 44 amu, which is referred to CO_2 molecules. The thermal curves indicate that the hydroxo compounds are decomposed with the evolution of nitrogen oxides in one step with a maximum at $T \sim 200$ °C.

Figure 3 shows the thermal curves and mass spectra of gases evolved during the calcination of the sample obtained using the deposition by precipitation of cobalt cations with a soda solution on δ - Al_2O_3 . Similar spectra were obtained for the sample prepared by the coprecipitation of the reactants. The DTG curve contains a broad endotherm related to the removal of adsorbed water at $T \leq 200$ °C and also a nonsymmetric effect with a maximum at $T \sim 310$ °C corresponding to the dehydroxylation of the hydroxo compound and CO_2 evolution. The mass spectrum of the evolved gases contains a narrow signal in the curve corresponding to a mass of 44 amu, which is attributed to CO_2 molecules, and two broad signals at 18 amu characteristic of water molecules. No signal corresponding to a mass of 30 amu is observed, indicating the absence of NO_3^- anions in the structure of precursor compounds. Thus, the cobalt–aluminum hydroxo compounds with the hydroxalcite structure obtained by the method considered is cobalt–aluminum hydroxocarbonate.

Composition of the hydroxo compounds obtained using the deposition by precipitation of cobalt cations with urea. The diffraction patterns of the precursor compounds ob-

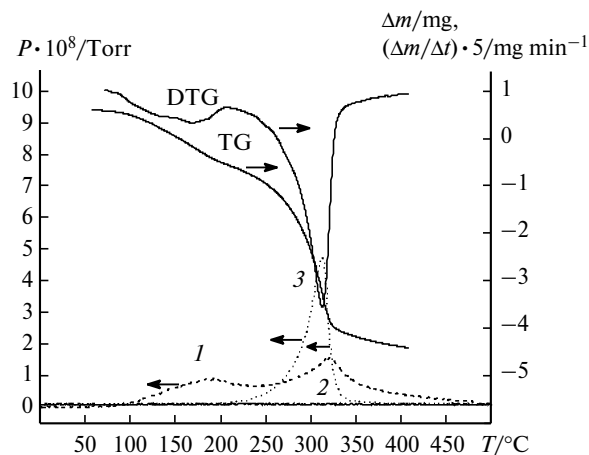


Fig. 3. Thermal curves in an argon medium and the mass spectra of the evolved gas for the sample obtained using the deposition by precipitation of cobalt cations with a soda solution on δ - Al_2O_3 (granule size 0.25–0.50 mm), Co : Al = 0.53 atomic fractions: MS = 18 (1), 30 (2), and 44 amu (3).

tained using deposition by precipitation with urea of cobalt cations on aluminum oxides are shown in Figs 4 and 5. The position of reflections and their intensity distribution correspond to the characteristics of the hydroxo compounds with the hydroxalcite-type structure. The hydroxalcite structure (described for the mineral $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) has a bilayer hexagonal packing of OH^- anions, whose octahedral cavities contain randomly distributed Mg^{2+} and Al^{3+} cations. Such brucite-like layers are bound by the carbonate anions and water molecules distributed in the interlayer space.⁴⁴ It is known⁴⁵ that a similar structure is retained upon the replacement of magnesium cations by copper, nickel, and cobalt cations.

The formation of the CoAl precursors with the hydroxalcite-type structure was observed for the Co/ γ - Al_2O_3 catalysts prepared from cobalt carbonate due to the treatment with an aqueous solution of citric acid.³⁷ The study

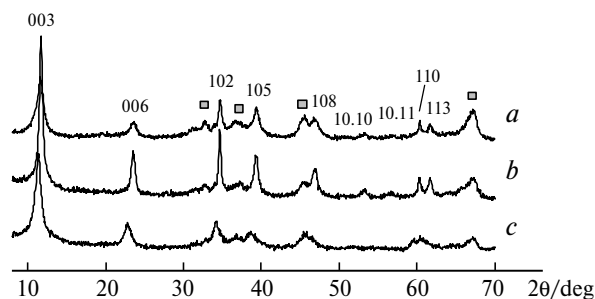


Fig. 4. Diffraction patterns of the precursor compounds obtained using the deposition by precipitation of cobalt cations with urea on δ - Al_2O_3 for the samples with the ratio Co : Al = 0.12 (a), 0.22 (b), and 0.43 atomic fractions (c). Reflection indices (hkl) for the hydroxalcite type structure are shown.

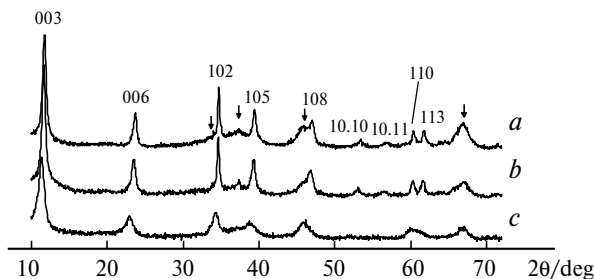


Fig. 5. Diffraction patterns of the precursor compounds obtained using the deposition by precipitation of cobalt cations with urea on γ -Al₂O₃ for the samples with the ratio Co : Al = 0.14 (a), 0.29 (b), and 0.33 atomic fractions (c). Reflection indices (*hkl*) for the hydrotalcite type structure are indicated.

of the Co/ γ -Al₂O₃ catalysts showed that the deposition by precipitation of cobalt cations from a nitrate solution on γ -Al₂O₃ with an ammonia solution resulted in the formation of the hydroxo compound of the hydrotalcite type with water molecules and nitrate and carbonate anions distributed in the interlayer space.³⁶

The thermal curves and mass spectra of the gas evolved upon the calcination of the samples with the composition Co : Al = 0.22 and 0.38 atomic fractions, which were obtained using the deposition by precipitation with urea of cobalt cations on δ -Al₂O₃ are shown in Fig. 6. The thermal transformation is accompanied by the evolution of water (18 amu), nitrogen oxide (30 amu), and carbon dioxide (44 amu). The signal corresponding to water evolution is broad with rather distinct division into two steps: water desorption and subsequent dehydroxylation of the hydroxo compound. The signal corresponding to the evolution of nitrogen oxide is symmetric for all prepared samples, and its intensity depends on the composition of the sample. The shape of the signal corresponding to the evolution of CO₂ indicates decomposition in two steps. The ratio of signal intensities corresponding to these steps and their integral intensity depend on the composition of the sample.

The mass spectrometric data on the ratio of integral intensities of the effects in the mass spectrometric curves of gas evolution at 18, 30, and 44 amu make it possible to estimate the ratio of anions OH⁻, NO₃⁻, and CO₃²⁻ in the precursors of the catalysts. These results are given in Table 2. As can be seen from the data in Table 2, the NO₃⁻/CO₃²⁻ ratio ranges from ~0.2 to ~8.5.

Thus, the hydroxo compounds with the structure of the hydrotalcite type prepared by the method described above represent cobalt–aluminum hydroxonitrate carbonates with various contents of the NO₃⁻ and CO₃²⁻ anions (see Table 2).

Influence of the method of preparation on the composition of the sample. It follows from the presented results that the method of preparation of the Co–Al catalysts by the deposition of cobalt cations on both γ -Al₂O₃ and δ -Al₂O₃

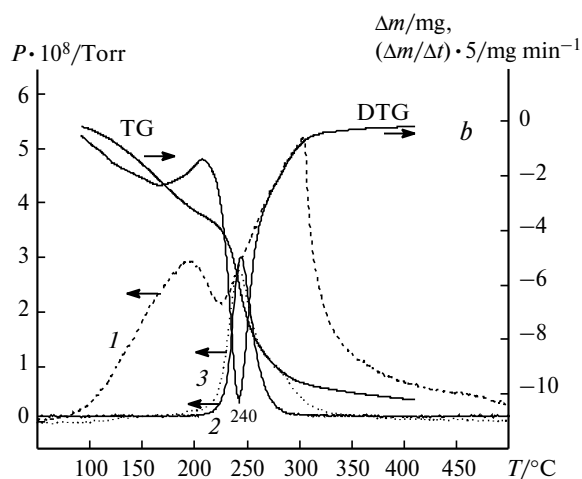
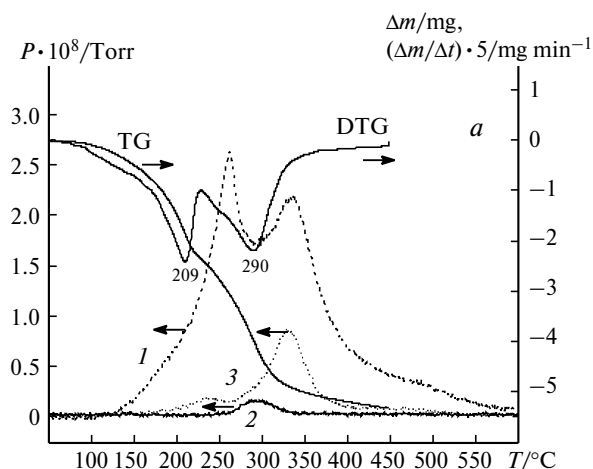


Fig. 6. Thermal curves in an argon medium and the mass spectra of the evolved gas for the samples obtained using the deposition by precipitation of cobalt cations with urea on δ -Al₂O₃ (size 0.25–0.50 mm), Co : Al = 0.22 (a), 0.38 atomic fractions (b); MS = 18 (1), 30 (2), and 44 amu (3).

determines the anionic composition and structure of the hydroxo compounds formed.

The study of the phase and chemical compositions of the prepared samples showed that the impregnation under the conditions used did not result in the interaction of the cobalt cations and aluminum oxides to form a combined compound: only crystalline hydrates of cobalt nitrate Co(NO₃)₂ · 4H₂O and Co(NO₃)₂ · 6H₂O were formed on the support surface.

The deposition by precipitation of cobalt cations on aluminum oxides with a soda solution leads to the formation of Co–Al hydroxocarbonate of the hydrotalcite type structure and some amount of cobalt hydroxocarbonate on the support surface.

The deposition by precipitation with urea of cobalt cations on aluminum oxides results in the formation on the support surface of Co–Al hydroxonitrate carbonate with the hydrotalcite type structure in which the ratio of

Table 2. Anionic composition of the precursor hydroxo compounds by the mass spectrometric data of gaseous products of the products of the thermal decomposition of the aluminocobalt systems

Sample	Anionic composition		
	$\text{NO}_3^-/\text{CO}_3^{2-}$	$\text{H}_2\text{O}/\text{CO}_3^{2-}$	$\text{H}_2\text{O}/\text{NO}_3^-$
1	1.60	15.0	9.0
2	0.22	6.5	30.0
3	8.40	25.0	3.0
4	0.42	8.7	20.0
5	3.10	14.0	4.0
6	0.67	6.4	10.0
7	0.19	5.3	28.0
8	0.22	9.1	41.0
9	0.57	5.4	9.0
10	0.40	7.7	19.0
11	1.90	8.9	5.0
12	0.92	6.9	7.0
13	3.80	14.0	4.0
14	2.10	21.0	10.0
15	6.40	2.9	0.5
16	0	2.1	—
17	0	4.5	—
19	35.0	54.0	1.6

* For the conditions of synthesis of the samples, see Table 1.

nitrate and carbonate anions is determined by the synthesis conditions.

The structures of Co—Al hydroxocarbonate and Co—Al hydroxonitrate carbonate are similar to that of hydrotalcite and differ in the anionic composition only.

Let us consider the data on the anionic composition of the hydroxonitrate carbonates obtained in the process of deposition by precipitation with urea of cobalt cations on the support γ - or δ - Al_2O_3 having the granule size 2.7×5.0 mm and 0.25 – 0.50 mm (see Table 1). It can be noted that, under other equivalent conditions of the synthesis (such as the concentration of reactants, temperature, and duration of hydrolysis), the ratio of the nitrate and carbonate groups is higher for larger granules of the support. This is probably related to differences in diffusion of the reactants. It is most likely that the deposition by precipitation with urea of cobalt cations on alumina proceeds in two steps: surface Co—Al hydroxonitrate is formed first and then the nitrate groups are partially replaced by the carbonate groups.

Catalytic properties of the Co—Al catalysts in the Fischer—Tropsch synthesis. The catalytic properties of the Co—Al catalysts obtained by the thermal treatment of the precursor compounds in an argon flow at 250 – 270 °C and then reduced in a hydrogen flow at 600 °C were studied at 210 °C and pressures of 1 and 21 atm.

The plot of the specific catalytic activity in CO hydrogenation vs ratio of the $\text{NO}_3^-/\text{CO}_3^{2-}$ anions in the hydroxo

compound of the catalyst precursor obtained under a pressure of 1 atm is shown in Fig. 7. It is seen that the catalysts, whose precursor compounds contain Co—Al hydroxocarbonates are poorly active, although the hydroxo compound obtained by the coprecipitation of the reactants exhibits somewhat higher activity.

The catalysts, whose precursor compounds contain Co—Al hydroxonitrate carbonates, are substantially more active and characterized by the following dependence of the activity on the ratio of the $\text{NO}_3^-/\text{CO}_3^{2-}$ anions. In the region of low contents of the nitrate anion ($\text{NO}_3^-/\text{CO}_3^{2-} < < -0.7$), the catalysts obtained using γ - and δ - Al_2O_3 differ in activity and the character of the dependence of the activity on the ratio of the $\text{NO}_3^-/\text{CO}_3^{2-}$ anions. At the ratio $\text{NO}_3^-/\text{CO}_3^{2-} = 0.2$ – 0.7 , the catalysts based on δ - Al_2O_3 manifest a higher activity, which decreased, nevertheless with an increase in the ratio of the $\text{NO}_3^-/\text{CO}_3^{2-}$ anions. However, the catalysts based on γ - Al_2O_3 with the anion ratio equal to 0.2 – 0.7 show a substantially lower activity, but it increases with an increase in the anion ratio and at $\text{NO}_3^-/\text{CO}_3^{2-} \sim 1$ the activities of the catalysts on γ - and δ - Al_2O_3 become similar. The activities of the catalysts remain almost at the same level with the further increase in the anion ratio and they somewhat decrease at $\text{NO}_3^-/\text{CO}_3^{2-} > \sim 7$. This difference in the activity of the catalysts based on γ - and δ - Al_2O_3 is due, most likely, to different dispersions of the hydroxo compounds formed on the surface of these supports.

The activity of the impregnated sample is several times lower than that of the sample deposited by precipitation with soda.

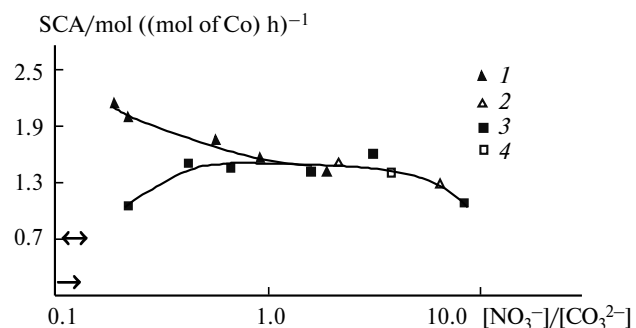


Fig. 7. Catalytic activity in the Fischer—Tropsch synthesis ($P = 1$ atm, $T = 210$ °C, $\text{CO} : \text{H}_2 : \text{N}_2 = 3 : 6 : 1$) vs ratio of the anions $\text{NO}_3^-/\text{CO}_3^{2-}$ in the composition of the precursors of the Co—Al catalysts obtained using the deposition by precipitation of cobalt cations with urea on alumina: 1, δ - Al_2O_3 (size 0.25 – 0.50 mm); 2, δ - Al_2O_3 (size 2.7×5.0 mm); 3, γ - Al_2O_3 (size 0.25 – 0.50 mm); and 4, γ - Al_2O_3 (size 2.7×5.0 mm). Symbols \rightarrow and \leftrightarrow mark the values of activity of the samples prepared using the deposition by precipitation of cobalt cations and the coprecipitation of the reactants with a soda solution, respectively; SCA is the specific catalytic activity expressed as the rate of CO conversion per unit of the cobalt amount in the sample.

At $P = 1$ atm the conversion of CO was 10–20%, selectivities of the studied catalyst to methane and hydrocarbons (C_{5+}) were 11–12% and 72–77%, respectively, the value of parameter α in the Anderson–Schulz–Flory molecular weight distribution (α_{ASF}) determined by the examination of the condensate to the content of C_{11} – C_{18} was 0.78–0.83, and selectivity to CO_2 did not exceed 0.05%. An insignificant amount of alcohols C_1 – C_4 was also observed in the reaction products.

The dependence of selectivity to hydrocarbons, $S_{C_{5+}}$, on the ratio of anions NO_3^-/CO_3^{2-} in the precursor of the catalyst obtained using the deposition by precipitation with urea of cobalt on the support at a pressure of 21 atm is shown in Fig. 8. The data in Fig. 8 show that the value of selectivity $S_{C_{5+}}$ increases with an increase in the relative content of the nitrate anion.

It is difficult to explain yet why the content of nitrate anions in the composition of the Co–Al hydroxo compounds (precursors) exerts a significant effect on the activity of the catalysts of the Fischer–Tropsch synthesis. However, it can be assumed that the NO_3^- anions control the oxidation state of the cobalt cations during the calcination of the hydroxo compounds and thus affect the particle size of metallic cobalt during activation. Probably, the presence of the NO_3^- anions prevents the formation of poorly reducible cobalt aluminate.

Thus, the formation of the active state of the cobalt-containing catalysts is completed by the activation of the catalyst in a medium favoring the reduction of cobalt to the finely dispersed metal. The data presented above indicate that the catalytic activity of the Co–Al catalysts can be controlled at the first step of preparation. At this step, the catalyst precursors are formed, whose anionic composition affects the catalytic properties of the precursors of the Co–Al catalysts.

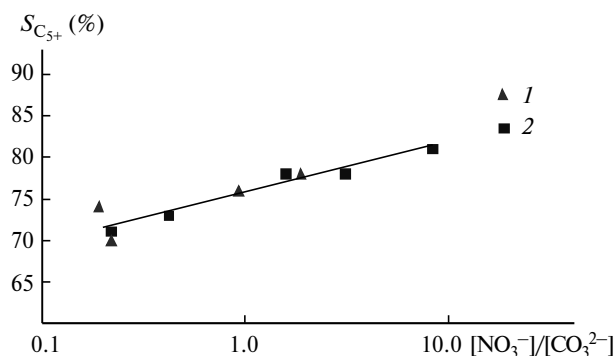


Fig. 8. Selectivity to hydrocarbons ($S_{C_{5+}}$) vs ratio NO_3^-/CO_3^{2-} in the composition of the precursors of the Co–Al catalysts obtained using the deposition by precipitation of cobalt cations with urea on alumina: 1, δ -Al₂O₃ (size 0.25–0.50 mm); 2, γ -Al₂O₃ (size 0.25–0.50 mm). The data were obtained in the Fischer–Tropsch synthesis at $P = 21$ atm, $T = 210$ °C, and $CO : H_2 : N_2 = 3 : 6 : 1$.

From the results of the study outlined above the following conclusions can be drawn.

1. The conditions for the preparation of the precursor compounds of the Co–Al catalysts by the deposition of cobalt cations on both γ -Al₂O₃ and δ -Al₂O₃ determine the anionic composition and structure of the formed hydroxo compounds.

2. The deposition of cobalt cations on aluminum oxides by impregnation results in the formation of crystalline hydrates of cobalt nitrates rather than the common cobalt and aluminum hydroxo compounds.

3. The precursor compounds of the aluminocobalt catalysts prepared using the deposition by precipitation of cobalt cations on the support or by the coprecipitation of cobalt and aluminum cations with soda solutions represent a mixture of aluminum oxides, cobalt hydroxocarbonate, and hydroxo compounds with the hydrotalcite-type structure.

4. The precursors obtained using the deposition by precipitation with urea of cobalt cations on aluminum oxides represent a mixture of aluminum oxides and hydroxo compounds with the hydrotalcite type structure.

5. The anionic composition of the cobalt–aluminum hydroxo compound depends on the method of preparation: the deposition of precipitation with a soda solution of cobalt cations on aluminum oxides, as well as the coprecipitation of the components with a soda solution, makes it possible to obtain Co–Al hydroxocarbonate on the support surface; the deposition by precipitation with urea of cobalt cations on aluminum oxides affords Co–Al hydroxonitrate carbonate; and the ratio of nitrate and carbonate anions is determined by the synthesis conditions.

6. The relationship between the catalytic properties of the Co–Al catalysts and the anionic composition of the hydroxo compounds in the catalyst precursors was revealed: the catalysts based on the precursor compounds containing Co–Al hydroxonitrate carbonate show higher activity compared to the catalysts based on the precursor compounds containing Co–Al hydroxocarbonate.

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