ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 4, pp. 497–503. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © I.I. Simentsova, A.A. Khassin, T.P. Minyukova, L.P. Davydova, A.N. Shmakov, O.A. Bulavchenko, S.V. Cherepanova, G.N. Kustova, T.M. Yurieva, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 4, pp. 520–526.

Effect of the Composition and Structure of the Precursor Compound on the Catalytic Properties of Cobalt–Aluminum Catalysts in the Fischer–Tropsch Synthesis

I. I. Simentsova[a, b], A. A. Khassin[a, b], T. P. Minyukova[a, b], L. P. Davydova[a], A. N. Shmakov[a, b], O. A. Bulavchenko[a], S. V. Cherepanova[a, b], G. N. Kustova[a], and T. M. Yurieva[a]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
e-mail: sii@catalysis.ru

Received November 29, 2011

Abstract—The effect of preparation procedure on the anionic composition and structure of hydroxo compounds as precursors of Co–Al catalysts and on their catalytic properties in the Fischer–Tropsch synthesis was studied. The dynamics of changes in the composition and structure of the hydroxide precursors of Co–Al catalysts during thermal treatment and subsequent activation was studied by thermal analysis, IR spectroscopy, XRD analysis, and in situ XRD analysis with the use of synchrotron radiation. It was found that the precursor compounds prepared by deposition–precipitation of cobalt cations on γ- and δ-Al_2O_3 under urea hydrolysis conditions, which had a hydrotalcite-type structure and contained nitrate, carbonate, and hydroxyl groups, turtned into the oxide compounds $Co_{3-x}Al_xO_4$ ($0 < x < 2$) with the spinel structure in the course of thermal treatment in an inert atmosphere. The hydrogen activation of an oxide precursor led to the formation of cobalt metal particles through the intermediate formation of a cobalt(II)–aluminum oxide phase. The catalyst was characterized by high activity and selectivity for C_{5+} hydrocarbons in the Fischer–Tropsch synthesis.

DOI: 10.1134/S002315841204012X

INTRODUCTION

The synthesis of olefins, liquid hydrocarbons, and ceresins from hydrogen-enriched synthesis gas, which is produced by the conversion of natural gas or associated petroleum gas, is most effectively performed with the use of cobalt-containing catalysts. According to published data, the activity of Co-containing catalysts depends on the conditions of their synthesis, in particular, on the composition of salts used in their preparation [1–5]. It was found that the samples prepared from the solutions of cobalt nitrates exhibited the greatest activity in the Fischer–Tropsch synthesis (FTS) [6, 7].

Recently, Simentsova et al. [8] found that, in addition to the composition of the parent cobalt salt, the methods of the interaction of catalyst components exert a considerable effect on the properties of the catalyst. In particular, various Co–Al compounds, which exhibit different catalytic properties in CO hydrogenation (FTS), are prepared by the impregnation of γ- or δ-Al_2O_3 with a nitrate solution, the deposition by precipitation of cobalt with a sodium carbonate solution, and the deposition by precipitation of cobalt under the urea hydrolysis conditions. Consequently, the properties of a catalyst that operates in the reducing atmosphere of hydrogenation reactions can be regulated at the first stage of its preparation—the stage of the production of hydroxo compounds. With consideration for the importance of the results obtained, this work was devoted to regulation of the catalytic properties of catalysts at the stage of the preparation of precursors. Attention was focused on the composition of hydroxo compounds formed by deposition by precipitation of cobalt cations on aluminum oxides under the urea hydrolysis conditions and upon the coprecipitation of cobalt and aluminum cations with a sodium carbonate solution. The dynamics of changes in the structure of the hydroxo compounds under the conditions of thermal treatment and the subsequent activation was studied. IR spectroscopy, X-ray diffraction (XRD) analysis, in situ XRD analysis with the use of synchrotron radiation, and thermogravimetry were used in this work.

EXPERIMENTAL

Preparation of Catalyst Samples

Solutions of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, pure grade) and the aluminum oxides γ-Al_2O_3 and δ-Al_2O_3, which were obtained by thermal treatment of aluminum hydroxide (Angarsk Catalysts and Organic Synthesis Plant JSC, trade mark A-64) in air at 700 and 910°C, respectively, for 2 h, were used in the synthesis of catalysts. The structure of the oxides was confirmed by X-ray diffraction analysis. The supports with granule sizes of 0.25–0.50 and 2.7 × 5.0 mm were used in the preparation of catalysts.

The catalysts were prepared by the thermal treatment in an inert gas flow of precursor compounds, which were aluminum oxide and the Co–Al hydroxo compound obtained by the deposition–precipitation of cobalt cations on aluminum oxide under the urea hydrolysis conditions.

The deposition by precipitation of cobalt cations under the urea hydrolysis conditions [9, 10] was performed as described below. The required amount of aluminum oxide was added to a solution of cobalt nitrate (0.047–3.4 mol/L) with stirring, and the mixture was heated to 90°C and kept under these conditions at a constant suspension volume for 23 h. After the completion of the synthesis, the sediment was separated from the mother liquor, washed with distilled water, and dried under an IR lamp at ~50°C for 10–15 h.

The coprecipitation (deposition by precipitation) of cobalt and aluminum cations with a solution of Na_2CO_3 was performed from 10% solutions of cobalt and aluminum nitrates (or on δ-Al_2O_3 with a granule size of 0.25–0.50 mm). The samples were coprecipitated at pH 7.3 ± 0.2 and a temperature of 65–70°C. The resulting precipitates were washed with distilled water for the removal of sodium to a concentration of no higher than 0.01 wt %.

Physicochemical Characterization of the Samples

The cationic composition of the samples was determined by atomic emission spectrometry using an Optima 4300 DV instrument.

Thermal analysis was carried out on a Netzsch STA-449 system in a flowing $H_2 : Ar = 50 : 50$ (vol %) mixture at a heating rate of 10 K/min. The gas flow rate was 150 mL/min.

The IR absorption spectra of the samples were obtained on a Bomem MB-102 Fourier transform spectrometer in the range of 250–4000 cm^{-1}. The samples were prepared as Vaseline oil mulls and were pressed into KBr pellets.

XRD analysis was performed on Bruker D8 and X'TRA diffractometers (Thermo Electron Corp., Switzerland) using CuK_α radiation with a monochromator in the reflected beam, and in situ XRD analysis was carried out on a precision X-ray diffractometer mounted in the synchrotron-radiation extraction channel of a VEPP-3 electron storage ring (at the Siberian Synchrotron and Terahertz Radiation Center). The precision X-ray diffractometer included a monochromator, a collimation system, and a position-sensitive detector. The single-reflection Ge(111) crystal monochromator deflected the monochromatic beam upward by ~30° in the vertical plane and afforded the degree of radiation monochromation $\Delta\lambda/\lambda \approx (2–3) \times 10^{-4}$. The operating radiation wavelength was $\lambda = 1.731$ Å. The diffractometer was equipped with an XRK-900 high-temperature reactor chamber (Anton Paar, Austria).

The sample was loaded in an open holder, which allowed the reaction mixture to penetrate the sample bulk, and was placed in the reactor chamber. The chamber was arranged on the diffractometer so that the monochromatic beam of synchrotron radiation was incident on the sample surface at an angle of ~15°.

The X-ray diffraction patterns of the catalyst were recorded in the 28°–60° range at a counting time of 1 min per data point. The rates of heating in the course of catalyst calcination in neon and reduction in hydrogen were 3–5 and 2 K/min, respectively. The gas flow rates were 1–1.5 mL/s. The sample was heated to 250°C in an inert atmosphere and was kept at this temperature for 1 h; then, it was cooled to 30°C and was reduced by heating to 700°C in hydrogen.

Catalytic Properties of Catalysts

The samples were studied in FTS reactions at a temperature of 210°C and pressures of 1 and 21 atm in an isothermal tubular flow reactor (3 mm in diameter) with a fixed bed of a granular catalyst in the case of the samples with a granule size of 0.14–0.25 mm (sample weight of 1 g) and in a single-row Temkin reactor [11] (4 mm in diameter) in the case of the samples with a granule size of 2.7 × 5.0 mm (sample weight of 4 g). The reaction mixture, whose composition was $CO : H_2 : N_2 = 30 : 60 : 10$ (vol %), was supplied at a pressure of 1 atm with a gas hourly space velocity (GHSV) of 2000–4000 h^{-1} (CO conversion of 10–20%) and at a pressure of 21 atm with a GHSV of 2000–6000 h^{-1} (CO conversion of 20–25%). The gas mixtures and condensate were analyzed on Tsvet-530 and Tsvet-560 chromatographs with flame-ionization detectors and a thermal-conductivity detector. The gas mixture components were separated on a capillary quartz column and a column packed with activated carbon; a capillary quartz column with an SE-54 stationary liquid phase was used in the separation of condensate components.

Catalytic studies were performed with samples that were precalcined in a flow of argon at 250–270°C and were then reduced in a flow of hydrogen at 600°C.

The specific catalytic activity expressed as CO conversion per unit time on the basis of the cobalt content of the catalyst was taken to be the measure of the activity of samples.

RESULTS AND DISCUSSION

Composition and Structure of Hydroxo Compounds: Dynamics of Their Changes in the Course of Thermal Treatment and Activation

Figure 1 shows the diffraction pattern of the hydroxide precursor of a cobalt–aluminum sample

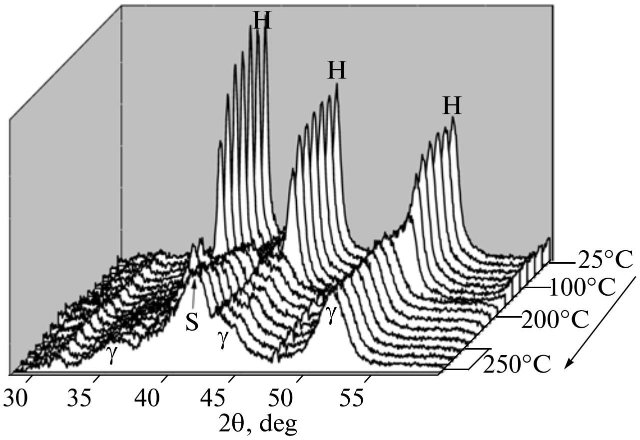

Fig. 1. In situ X-ray diffraction patterns of a sample with the cationic ratio Co : Al = 0.29 (atomic fractions) heated in a flow of neon. The sample was prepared by the deposition–precipitation of cobalt on γ-Al_2O_3 under the urea hydrolysis conditions. Reflections: H, hydrotalcite; S, spinel; γ, γ-Al_2O_3.

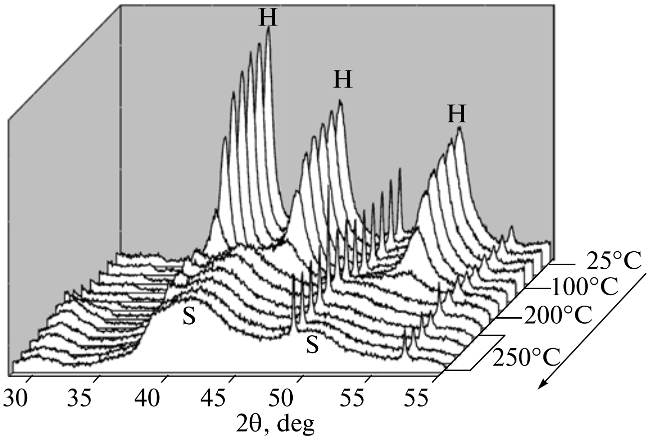

Fig. 2. In situ X-ray diffraction patterns of a sample with the cationic ratio Co : Al = 1 (atomic fractions) heated in a flow of neon. The sample was prepared by the coprecipitation of cobalt and aluminum with sodium carbonate. Reflections: H, hydrotalcite; S, spinel.

prepared by the deposition–precipitation of cobalt on γ-Al_2O_3 under the urea hydrolysis conditions, measured in situ on heating in an atmosphere of neon. The X-ray diffraction pattern of the initial sample exhibited reflections corresponding to the structures of hydrotalcite and the γ-Al_2O_3 support. On heating, the intensity of hydrotalcite peaks gradually decreased until their complete disappearance; the diffraction profile of aluminum oxide, whose peaks overlap with the peaks of hydrotalcite, became more clearly pronounced. Simultaneously, a peak at 41.7° appeared (interplanar spacing of $d = 2.43$ Å), which corresponds to the strongest (311) reflection of the structure of spinel $Co_{3-x}Al_xO_4$ ($0 < x < 2$). According to data obtained by in situ XRD analysis, the unit cell parameter of this oxide compound can be estimated at 8.084 ± 0.005 Å. The special-purpose recording of the XRD pattern demonstrated that the unit cell parameter is $a = 8.085 \pm 0.002$ Å, which is close to the reference value (8.086 Å) for Co_2AlO_4 [ICDD PDF 38-0814].

Figure 2 shows the diffraction pattern of the hydroxide precursor of the cobalt–aluminum sample prepared by the coprecipitation of cobalt and aluminum with sodium carbonate, recorded in situ on heating in an atmosphere of neon. It can be seen that this sample in the initial state also contained a phase with the hydrotalcite-type structure. In the course of heating in an inert atmosphere, a spinel-type cobalt–aluminum compound was formed with a unit cell parameter close to the value characteristic of the structure of Co_2AlO_4, as for the samples prepared under the urea hydrolysis conditions.

Thus, upon thermal treatment in an inert atmosphere, the initial hydroxo compounds with the hydrotalcite-type structure turned into cobalt–aluminum oxide compounds with the spinel-type structure.

Figure 3 shows the IR spectra of the initial hydroxo compounds (catalyst precursors) prepared by different methods: (1) the deposition of cobalt on various aluminum oxide modifications at different proportions of Co and Al cations and (2) the coprecipitation of cobalt and aluminum cations with sodium carbonate. In Fig. 3, it can be seen that the narrow absorption bands at 1384 cm^{-1}, which are characteristic of the vibrations of NO_3^--anions, were present in the spectra of the samples prepared under the urea hydrolysis conditions. In

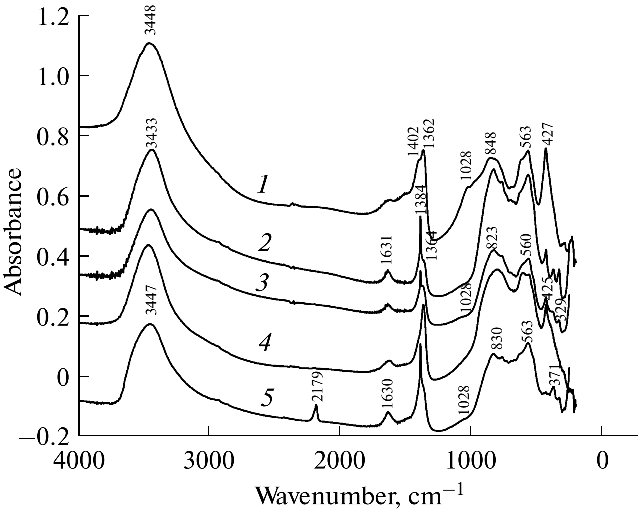

Fig. 3. IR spectra of the dry samples prepared by the deposition–precipitation of cobalt under the urea hydrolysis conditions: (*2*, *3*, and *5*) on δ-Al_2O_3 at the ratios Co : Al = 0.12, 0.22, and 0.43 (atomic fractions), respectively; (*4*) on γ-Al_2O_3 at the ratio Co : Al = 0.29 (atomic fractions). Sample *1* was prepared by the coprecipitation of cobalt and aluminum with sodium carbonate at the ratio Co : Al = 1 (atomic fractions).

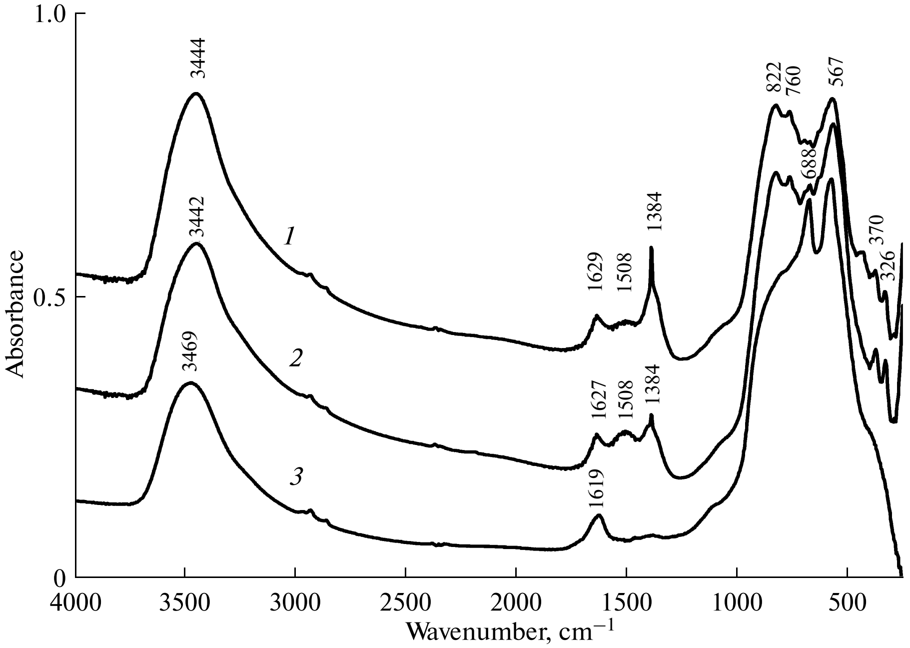

Fig. 4. IR spectra of the samples prepared by the deposition–precipitation of cobalt on (*1*, *2*) δ-Al_2O_3 and (*3*) γ-Al_2O_3 under the urea hydrolysis conditions and calcined in argon at (*1*) 180, (*2*) 240, and (*3*) 400°C. The ratio Co : Al = 0.22 or 0.29 (atomic fractions) for samples *1* and *2* or *3*, respectively.

the spectrum of the sample coprecipitated with sodium carbonate, only a shoulder at 1402 cm^{-1} and an absorption band at 1362 cm^{-1} due to vibrations within layer anions (CO_3^{2-}) can be seen; this is characteristic of layered structures of the hydrotalcite type [12, 13]. The sets of absorption bands at 1028 cm^{-1} and in the regions of 820–560 and 425–329 cm^{-1} correspond to the absorption of compounds with the structures of the hydrotalcite type and aluminum oxide.

Thus, the hydroxo compound precursors prepared by different methods contained the same phase with the hydrotalcite-type structure and different anionic compositions. In addition to carbonate anions, NO_3^--anions were present in the hydroxo precursors of the samples prepared by the deposition–precipitation of cobalt on the support under the urea hydrolysis conditions, whereas they were absent from the samples coprecipitated with sodium carbonate.

Upon thermal treatment in an inert atmosphere, the anionic composition of the hydroxo compounds prepared by the deposition–precipitation of cobalt on the support under the urea hydrolysis conditions changed with calcination temperature. Figure 4 shows the IR spectra of the samples after calcination in an atmosphere of argon at different temperatures. It can be seen that, at 180°C, some amount of nitrate anions remained in the catalyst; a narrow absorption band at 1384 cm^{-1} corresponds to these anions. At a calcination temperature of 240°C, the absorption band at 1384 cm^{-1} considerably decreased and completely disappeared after the calcination of the hydroxo precursor at 400°C. Unlike the hydroxo compounds, the oxide catalyst precursors did not contain nitrate groups in their composition. The presence of absorption bands in the region of 822–760 cm^{-1}, whichcorrespond to the vibrations of Al_2O_3, and in the regions of 668–567 and 370–326 cm^{-1}, which correspond to the absorption of spinel, does not contradict the data of structural studies on the formation of a Co–Al oxide compound like Co_2AlO_4 with the spinel structure in the course of calcination in an inert atmosphere.

Thus, the oxide precursors prepared by the deposition–precipitation of cobalt onto aluminum oxide under the urea hydrolysis conditions and calcined at 250–400°C in an inert atmosphere did not contain NO_3^- anions.

After thermal treatment, the samples were activated in a flow of a hydrogen-containing mixture or hydrogen. Figure 5 shows the results of the thermal analysis of the reduction of the cobalt–aluminum oxide precursors, which differed in the proportions of Co and Al cations, prepared by the deposition of cobalt onto γ- and δ-Al_2O_3 under the urea hydrolysis conditions. It can be seen that, regardless of the support modification, the reduction of samples at medium temperatures (above 200°C) occurred in two main steps with weight loss maximums at about 300 and 600°C. These transformations of the oxide precursors of the Co–Al catalysts can be related to the consecutive reduction of Co(III) to Co(II) and then to Co^0. In the figures, it can be seen that the last endotherm, which is due to the reduction of cobalt to the metal state, shifted to lower temperatures as the Co : Al ratio in the sample was increased. In the catalysts with the cationic ratios Co : Al = 0.33–0.43 (atomic fractions) (or containing 20–24 wt % cobalt), the reduction of cobalt to the metal came into play at temperatures of about 450°C.

Figure 6 shows the series of X-ray diffraction patterns obtained upon the in situ reduction of the Co–Al catalyst prepared with the use of γ-Al_2O_3 under the urea hydrolysis conditions and precalcined in an atmosphere of neon at 250°C. Initially, a small increase in the intensity of the peaks due to the spinel phase, which was likely due to the continuing oxide crystallization, was observed on heating from 50 to 200°C. At 230°C, the intensity of the spinel reflections decreased and a peak at 48.7° appeared, which may be indicative of the formation of an oxide compound like cobalt oxide with a simple cubic lattice. However, the interplanar spacing of this oxide was $d = 2.10$ Å, as evaluated from the reflection (200); this value is different from the tabulated value for CoO ($d_{CoO} = 2.13$ Å) [ICDD PDF 43-1004]. Because the oxide compound was formed from the cobalt–aluminum spinel, we believe that it was the cobalt(II)–aluminum oxide $Co_{1-x}Al_xO$. The decrease in the interplanar spacing can be a consequence of different ionic radii: the ionic radius of Co^{2+} in an octahedral environment is 0.65 Å, and that of Al^{3+} is 0.54 Å. As the reduction temperature was further increased, the $Co_{1-x}Al_xO$ phase gradually disappeared, and the reflection (111), which is due to cobalt metal, became noticeable at 580°C.

The particle size of the resulting metal was calculated from the most intense reflection (111) for Co^0. Figure 7 shows the changes in the size of the coherent scattering domain (CSD) of cobalt metal particles as a function of temperature. It can be seen that the size of CSD increased from 60 to 120 Å with increasing reduction temperature. The surface area of the well-crystallized cobalt metal particles on the surface of the catalysts reduced at 600°C was determined by titration with nitrous oxide. The specific surface area of Co^0 in the samples with the atomic ratios Co : Al = 0.22–0.29 was ~22 m^2/g, regardless of whether the support was γ- or δ-Al_2O_3.

Activity of the Catalysts in the Fischer–Tropsch Synthesis

The table summarizes the results of the catalytic studies of the samples prepared by the thermal treatment of hydroxo precursors in a flow of argon at 250–270°C and reduced in hydrogen at 600°C. The proportions of OH^-, NO_3^-, and CO_3^{2-} anions in the catalyst precursors were evaluated using mass-spectrometric data [8] on the ratios between the integrated intensities of effects in the mass-spectrometric curves of gas release for signals at m/z 18, 30, and 44.

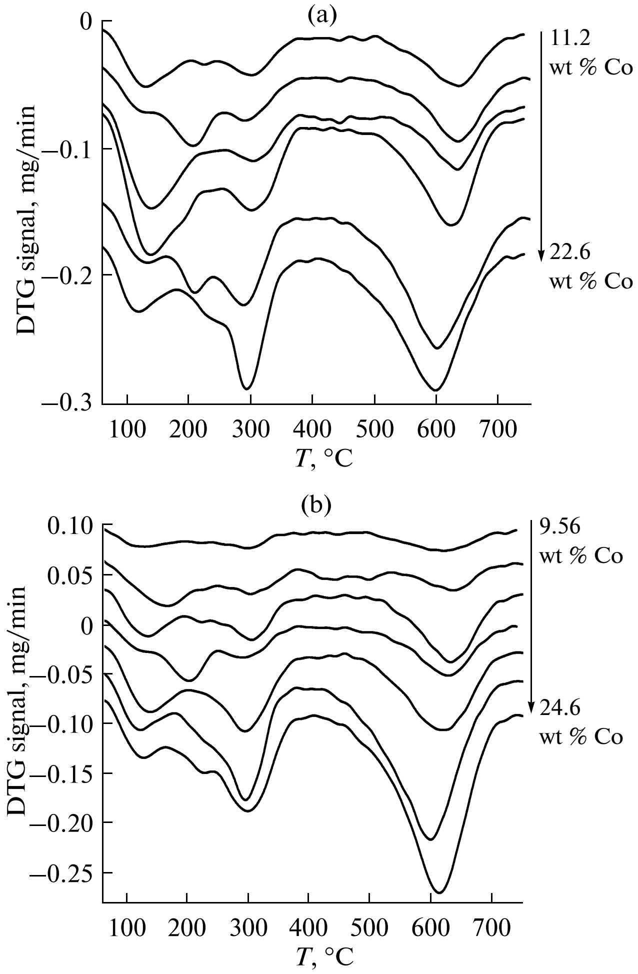

Fig. 5. Differential thermogravimetric curves for the reduction in a hydrogen-containing mixture of cobalt–aluminum samples prepared by the deposition–precipitation of cobalt on (a) γ-Al_2O_3 and (b) δ-Al_2O_3 under the urea hydrolysis conditions and precalcined in argon.

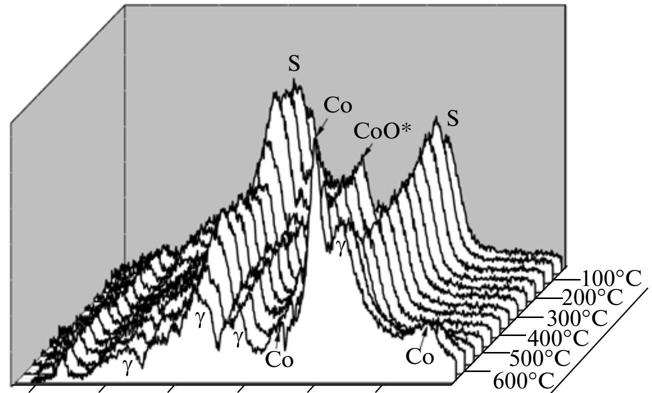

Fig. 6. In situ X-ray diffraction patterns obtained during the reduction of a catalyst prepared with the use of γ-Al_2O_3 with the ratio Co : Al = 0.29 (atomic fractions) under the urea hydrolysis conditions. The sample was precalcined at 250°C in neon. Reflections: S, spinel; CoO*, cobalt–aluminum oxide $Co_{1-x}Al_xO$; γ, γ-Al_2O_3; Co, cobalt metal.

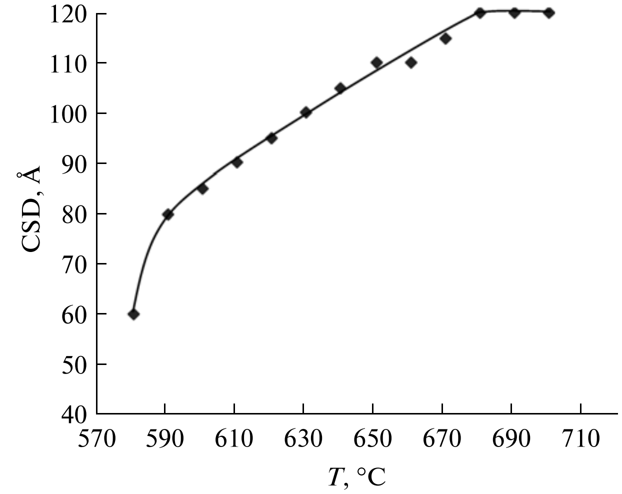

Fig. 7. CSD size of cobalt metal in the reduced sample prepared with the use of γ-Al_2O_3 under the urea hydrolysis conditions with the ratio Co : Al = 0.29 (atomic fractions) as a function of the catalyst reduction temperature.

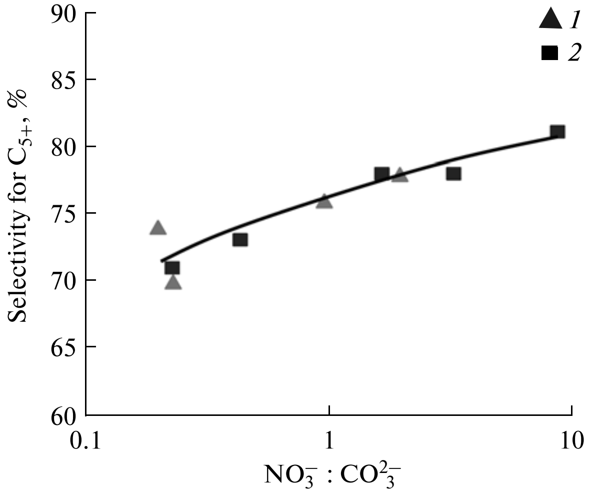

Fig. 8. Dependence of the selectivity of catalysts for C_{5+} in the Fischer–Tropsch synthesis on the anionic ratio $NO_3^- : CO_3^{2-}$ in hydroxo compounds. $P = 21$ atm; $T = 210°C$; CO : H_2 : N_2 = 3 : 6 : 1; CO conversion, 20–25%: (*1*) δ-Al_2O_3 (0.25–0.50 mm) and (*2*) γ-Al_2O_3 (0.25–0.50 mm).

The table indicates that the samples prepared by the deposition–precipitation of cobalt under the urea hydrolysis conditions whose precursor compounds were cobalt–aluminum hydroxo nitrate carbonates with the hydrotalcite-type structure were more active by a factor of >2 than the samples prepared by coprecipitation/deposition–precipitation with sodium carbonate whose precursors had the hydrotalcite-type structure, but they were cobalt–aluminum hydroxo carbonates.

Figure 8 shows the dependence of selectivity for C_{5+} hydrocarbons on the anionic ratio $NO_3^- : CO_3^{2-}$ in the composition of hydroxo compounds obtained by the deposition–precipitation of cobalt under the urea hydrolysis conditions at a pressure of 21 atm. As can be seen, an increase in the selectivity for C_{5+} was observed with an increasing relative concentration of the nitrate anion in the hydroxo precursor. It is believed that the presence of nitrate anions makes it possible to control

Activity of the catalysts in the Fischer–Tropsch synthesis (1 atm; 210°C; CO : H_2 : N_2 = 3 : 6 : 1)

Preparation procedure	Support (granule size, mm)	Co : Al (atomic fractions)	Anionic composition			Specific catalytic activity, (mol CO) (mol Co)$^{-1}$ h^{-1}
			NO_3^- : CO_3^{2-}	H_2O : CO_3^{2-}	H_2O : NO_3^-	
Supporting by precipitation under the conditions of urea hydrolysis	γ-Al_2O_3 (0.25–0.50)	0.30	0.4	8.7	20	1.5
	γ-Al_2O_3 (0.25–0.50)	0.40	0.7	6.4	10	1.4
	δ-Al_2O_3 (0.25–0.50)	0.40	1.9	8.9	5	1.4
	δ-Al_2O_3 (0.25–0.50)	0.20	0.2	5.3	28	2.1
	γ-Al_2O_3 (2.7 × 5.0)	0.10	3.8	13.9	4	1.4
	δ-Al_2O_3 (2.7 × 5.0)	0.20	6.5	2.9	2	1.3
Supporting by precipitation with soda	δ-Al_2O_3 (0.25–0.50)	0.50	0	2.1	–	0.3
Coprecipitation with soda	γ-Al_2O_3	1.00	0	4.5	–	0.7

the oxidation state of cobalt cations in the course of the thermal treatment of hydroxo compounds and, accordingly, to control the particle size of cobalt metal upon activation.

Thus, we experimentally observed a crucial effect of the preparation procedure on the anionic composition and structure of the hydroxo compound precursors of Co–Al catalysts and, as a consequence, on the catalytic properties in FTS reactions. The coprecipitation of cobalt and aluminum cations or the deposition by precipitation of cobalt cations onto aluminum oxides affords Co–Al hydroxo compounds with the hydrotalcite-type structure. However, the conditions of precipitation/deposition by precipitation radically influence the chemical composition of hydrotalcite and the subsequent formation of the catalyst in the course of thermal treatment and reductive activation.

The catalysts whose precursor compounds are Co–Al hydroxo nitrate carbonates with the hydrotalcite-type structure are the most active ones. The dependence of the activity on the structure of the oxide support was observed at low concentrations of nitrate anions ($NO_3^- : CO_3^{2-} < \sim 0.7$). Catalysts based on δ-Al_2O_3 exhibit better activity.

The catalysts whose precursor compounds contain Co–Al hydroxo carbonates are inactive. Note that the hydroxo compound obtained by the coprecipitation of reagents exhibits a somewhat higher activity.

During thermal treatment in an inert atmosphere, Co–Al hydroxo nitrate carbonates with the hydrotalcite-type structure turn into the oxide compounds $Co_{3-x}Al_xO_4$ ($0 < x < 2$) with the spinel-type structure. The hydrogen activation of the oxide precursor leads to the formation of cobalt metal particles through the intermediate formation of the cobalt(II)–aluminum oxide phase $Co_{1-x}Al_xO$. In the samples with the anionic ratio $0.2 < NO_3^- : CO_3^{2-} < 7.0$, cobalt metal particles with the CSD size of ~6–8 nm and a specific surface area of >20 m^2/g are formed. This catalyst is characterized by high activity and selectivity for C_{5+} hydrocarbons in the Fischer–Tropsch synthesis.

ACKNOWLEDGMENTS

We are grateful to G.A. Filonenko and G.K. Chermashentseva for their assistance.

This study was performed within the framework of project no. 4 of program no. 19 “Chemical Aspects of Power Engineering” of the Presidium of the Russian Academy of Sciences. The facilities of the Siberian Synchrotron and Terahertz Radiation Center were used in this study (state contract no. 16.552.11.7044).

REFERENCES

1. Bae, J.W., Kim, S.M., Kang, S.H., Chary, K.V.R., Lee, Y.J., Kim, H.J., and Jun, K.W., *J. Mol. Catal. A: Chem.*, 2009, vol. 311, nos. 1–2, p. 7.
2. Kraum, M. and Baerns, M., *Appl. Catal., A*, 1999, vol. 186, nos. 1–2, p. 189.
3. Girardon, J.S., Lermontov, A.S., Gengembre, L., Chernavskii, P.A., Griboval-Constant, A., and Khodakov, A.Y., *J. Catal.,* 2005, vol. 230, p. 339.
4. Girardon, J.S., Constant-Griboval, A., Gengembre, L., Chernavskii, P.A., and Khodakov, A.Y., *Catal. Today,* 2005, vol. 106, p. 161.
5. Sun, S., Tsubaki, N., and Fujimoto, K., *Appl. Catal., A*, 2000, vol. 202, no. 1, p. 121.
6. Oukaci, R., Singleton, A., and Goodwin, J.G., Jr., *Appl. Catal., A*, 1999, vol. 186, p. 129.
7. Espinoza, R.L., Steynberg, A.P., Jager, B., and Vosloo, A.C., *Appl. Catal., A*, 1999, vol. 186, p. 13.
8. Simentsova, I.I., Khassin, A.A., Filonenko, G.A., Chermashentseva, G.K., Bulavchenko, O.A., Cherepanova, S.V., and Yurieva, T.M., *Russ. Chem. Bull.*, 2011, vol. 60, no. 9, p. 1827.
9. Van der Grift, C.J.G., Elberse, P.A., Mulder, A., and Geus, J.W., *Appl. Catal.,* 1990, vol. 59, p. 275.
10. Bezemer, G.L., Radstake, P.B., Koot, V., Dillen, A.J., Geus, J.W., and Jong, K.P., *J. Catal.,* 2006, vol. 237, no. 2, p. 291.
11. Bodrov, I.M., Apel’baum, L.O., and Temkin, M.I., *Kinet. Katal.,* 1964, vol. 5, no. 4, p. 696.
12. Frost, R.L. and Erickson, K.L., *Spectrochim. Acta, Part A*, 2004, vol. 60, no. 13, p. 3001.
13. Perez-Ramirez, J., Mul, G., Kapteijn, F., and Moulijn, J.A., *Mater. Res. Bull.*, 2001, vol. 36, p. 1767.