Russian Chemical Bulletin, International Edition, Vol. 60, No. 9, pp. 1835—1841, September, 2011

Nature of active sites in the cobalt—zirconium oxide catalyst

D. A. Grigoryev[a] *and M. N. Mikhailov*[a,b★]

[a]*United Research and Development Center,*
Building 2, 55/1 Leninsky prosp., 119333 Moscow, Russian Federation
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 730 6102. E-mail: mik@ioc.ac.ru

The temperature-programmed reduction, powder X-ray diffraction, and oxygen adsorption methods were applied to study the phase composition and the nature of the active surface of the catalyst Co(10%)/ZrO_2. The results of the physicochemical studies were compared with the data on the activity and selectivity of the catalysts in the synthesis of hydrocarbons from CO and H_2. The mechanism for the reduction of the cobalt phases in the Co(10%)/ZrO_2 system was proposed. The main features governing the formation of active sites of the synthesis of high-molecular-weight hydrocarbons were considered.

Key words: cobalt-based catalyst, Fischer—Tropsch synthesis, zirconia, catalyst activation, active sites.

The Fischer—Tropsch synthesis is an important stage in casing-head gas utilization and transportation of natural gas. The key factor of this process is the selection of an optimal catalyst, which determines the yield and composition of hydrocarbon products.[1] The most part of catalysts of the Fischer—Tropsch synthesis contain cobalt compounds immobilized on the support. One of the main steps in formation of the active phase of the cobalt catalysts is reductive activation necessary for the reduced cobalt catalysts to be formed on the catalyst surface.[2] The supports used for the catalysts of the Fischer—Tropsch synthesis are not inert materials and during preparation and activation they can form poorly reducible compounds of cobalt. These compounds decrease the activity of the catalyst.[3] It is known that the active sites of the classical catalysts of the Fischer—Tropsch synthesis contain cobalt atoms in two different states: as metallic particles and cations of the oxide formed due to the strong interaction of cobalt oxide with the oxide support, *viz.*, $Co^{\delta+}$—$CoO \cdot M_xO_y$.[4,5] For example, in the presence of the classical catalysts of the Fischer—Tropsch synthesis Co/Al_2O_3, spinel structures are formed and the cobalt atoms (a part of them) become inactive in catalysis. In addition, the reduction of the cobalt catalysts on the classical supports (aluminum, silicon, and titanium oxides) require high temperatures (400—500 °C). Therefore, one of the main directions of improvement of the Fischer—Tropsch synthesis is the development of catalytic systems characterized by a weak metal—support interaction. No poorly reducible cobalt zirconates are formed in the Co/ZrO_2 catalysts. It has recently been shown[6] that in the Co/ZrO_2 system the active component is reduced so easily that metallic cobalt is already formed at the synthesis temperature (250 °C). ZrO_2 is not characterized by a strong interaction with cobalt oxide and, hence, it is of interest to reveal the nature of active sites of the Co/ZrO_2 catalysts and their relationship to the formation of solid solutions Co—O—Zr (see Ref. 7) for the isomorphic substitution of the Zr atoms by the Co atoms.[8] For this purpose, we prepared a series of catalysts Co(10%)/ZrO_2 and studied their properties under various conditions of preliminary activation by the temperature-programmed reduction (TPR), powder X-ray diffraction analysis, and oxygen adsorption method.

Experimental

The tetragonal modification of zirconia was used as a support. The procedure for preparation of support granules and their physicochemical characteristics have earlier been described.[6] Cobalt was introduced into the catalyst by the impregnation of the support with an aqueous solution of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (10 wt.%). After impregnation, the catalysts was calcined for 1 h at 270 °C in air.

Powder X-ray diffraction analysis was carried out on a Dron-3 diffractometer. The samples were scanned at a rate of 0.5 °C min^{-1} using Cu-Kα radiation and cerium oxide as an internal standard, which was introduced in an amount of 10 wt.% with respect to the sample weight.

The temperature-programmed reduction of the freshly calcined catalysts and the samples subjected to preliminary activation in hydrogen (weighed sample 250 mg) was carried out on an AutoChem II 2920 instrument (Micromeritics) in a flow (10 mL min^{-1}) of the H_2 (5%) + Ar (95%) gas mixture. The

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1804—1810, September, 2011.

temperature was linearly increased from 100 to 900 °C with a rate of 10 °C min^{-1}.

Oxygen adsorption on the samples pre-activated in hydrogen (weighed sample 300 mg) was carried out on an AutoChem II 2920 instrument (Micromeritics). After reduction, the sample surface was purified from weakly sorbed compounds with a helium flow (30 mL min^{-1}) for 60 min and the sample was cooled down to ~20 °C. Then the low-temperature (at –110 °C) and high-temperature (at 450 °C) titration with oxygen was performed. For this purpose, oxygen from the loop (volume 1 mL) swept with the O_2 (15%) + He (85%) mixture was introduced by impulses into a helium flow (60 mL min^{-1}) that was passed through the weighed sample. The degree of reduction of oxygen was calculated on the basis of the assumption that the oxidation proceeds according to the stoichiometric equations to Co_3O_4

$$3\,Co^0 + 2\,O_2 \longrightarrow Co_3O_4,$$

$$3\,CoO + 0.5\,O_2 \longrightarrow Co_3O_4.$$

Using the low-temperature adsorption of oxygen, the dispersity and surface area of metallic cobalt were calculated accepting that each cobalt atom adsorbs one oxygen molecule. The size of crystallites of metallic cobalt was determined assuming that the cobalt crystallites were spherical and did not interact with the support

$$d = \frac{6V_{Co}}{S_{Co}} = \frac{6\lambda R_{Co}\cdot 0.01^2}{\rho_{Co}Ad_{O_2}N_A S_0},$$

where ρ_{Co} is the density of metallic Co equal to 8.9 g cm^{-3}; λ is the Co content in the catalyst, wt.%; R_{Co} is the degree of reduction of Co, %; m is the catalyst weight, g; 0.01 is the coefficient of recalculation of the values expressed in percents to the value in weight fraction; $N_A = 6.02\cdot10^{23}$ is Avogadro´s number; $S_0 = 0.66225\cdot10^{-19}$ is the average surface area per one surface cobalt atom, m^2; and Ad_{O2} is the low-temperature amount adsorbed of oxygen in μmol g^{-1}.

Microcatalytic experiments were carried out in a steel tubular reactor (inner diameter 12 mm) on a flow-type catalytic setup. The conditions of the process were as follows: P = 2 MPa, $H_2 : CO : N_2 = 63 : 31.5 : 5.5$ (vol.%). The catalysts reduced with hydrogen and the catalyst that was not preliminarily subjected to reductive treatment were activated in a synthesis gas flow (volumetic flow rate 1000 h^{-1}). The catalyst was heated to 170 °C with a rate of 2 °C min^{-1}. Then the temperature of the process was increased stepwise until the conversion of carbon monoxide reached a value >70%.

The initial mixture and gaseous synthesis products were analyzed by gas adsorption chromatography using a thermal conductivity detector and helium as a carrier gas. Molecular sieves CaA (3 m × 3 mm) served as the first column, and the second column was HayeSep. The first column was used for the analysis of CO and N_2 (isothermal regime, 80 °C), whereas CO_2, CH_4, and hydrocarbons C_2—C_4 were analyzed on the second column (temperature-programmed regime, 80—200 °C, 8 °C min^{-1}). The composition of the liquid synthesis products was determined by gas liquid chromatography using a flame-ionization detector and helium as a carrier gas. A capillary column (50 m) with the DB-Petro 0.5 stationary phase was used for analysis (temperature-programmed regime, 50—250 °C, 3 °C min^{-1}).

Results and Discussion

The powder X-ray diffraction patterns of the calcined catalyst Co(10%)/ZrO_2 and the samples activated at 250 °C for 1 and 24 h and at 350 °C for 1 h are presented in Fig. 1. The X-ray diffraction pattern of the unreduced sample exhibits lines due to the oxide phase Co_3O_4 (see Fig. 1, curve *a*). The activation of the catalysts at both 250 and 350 °C leads to the complete disappearance of the lines of the crystalline phase Co_3O_4 (see Fig. 1, curves *b*—*d*), which is caused by the complete reduction of this phase to form the cobalt phases amorphous to X-rays. It was shown[9] by the powder X-ray diffraction study of the Co/ZrO_2 systems that the Co_3O_4 phase disappeared and the CoO phase appeared upon hydrogen reduction at temperatures higher than 200 °C. All diffraction peaks disappear from the X-ray diffraction patterns after activation at 300 °C. This can be explained by the fact that in the temperature range from 200 to 300 °C bulk CoO is transformed into the amorphous oxide phase or reduced to the amorphous phase of metallic cobalt. The lines of the bulk phase of metallic cobalt appeared in the X-ray diffraction patterns of the reduced samples only upon the activation at $T > 400$ °C.[10]

An analysis of the TPR curves gives more complete data on the state of cobalt in the catalysts. The TPR curves of the calcined and pre-activated in hydrogen samples are given in Fig. 2. Three peaks can be distinguished in the TPR spectrum of the calcined Co(10%)/ZrO_2 sample (see Fig. 2, curve *a*). The first peak at 195—250 °C with a maximum at 225 °C corresponds to the reduction of oxide Co_3O_4 to CoO.[11] The second peak with a maximum at 350 °C can be assigned to the reduction of CoO to metallic cobalt.[12] The third broad peak at 420—670 °C

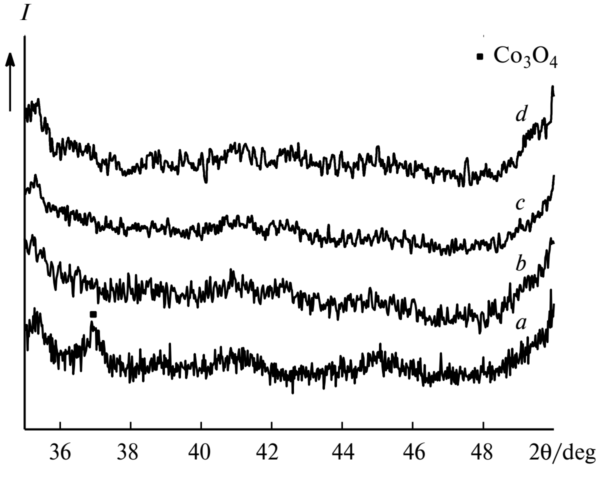


Fig. 1. Powder X-ray diffraction patterns of the samples of the Co(10%)/ZrO_2 catalyst calcined at 270 °C (*a*) and reduced with hydrogen at 250 °C for 1 h (*b*), at 250 °C for 24 h (*c*), and at 350 °C for 1 h (*d*).

with a maximum at 565 °C reflects the reduction of surface cobalt oxides[13] weakly interacting with zirconia[14] to form the metal. A shoulder of the peak at 665—750 °C is observed in the TPR curve of the calcined sample. It was suggested[15] that this peak corresponds to the recrystallization of the support (transition from the metastable tetragonal to monoclinic phase[16]) and reduction of solid solutions Co—O—Zr (see Ref. 17). Compared to the $Co(10\%)/ZrO_2$ sample calcined at 400 °C,[6] the peaks in the TPR spectrum of the catalyst heated at 270 °C are shifted to low temperatures. A decrease in the temperature of preliminary treatment of the catalyst increases the dispersity of oxide Co_3O_4.[18] For the Co/ZrO_2 system due to the weak metal—support interaction, an increase in the dispersity leads to an increase in the reduction ability of the catalyst,[14] whereas for the Co/Al_2O_3 catalyst an increase in the dispersion of cobalt oxide favors the formation of spinel structures and deteriorates the reduction properties.[19]

The degree of cobalt reduction in the activated catalyst was estimated from the value of the surface area under the TPR curve for the calcined and reduced $Co(10\%)/ZrO_2$ samples using the formula

$$R_{Co}{}^{T,\tau}(\%) = \frac{S(\mathrm{TPR}) - S(\mathrm{TPRR}(T,\tau))}{S(\mathrm{TPR})} \cdot 100\%,$$

where $R_{Co}{}^{T,\tau}$ is the degree of reduction of cobalt activated with hydrogen at temperature T and time τ; S(TPR) is the surface area under the curve of the TPR spectrum of the calcined catalyst; and $S(\mathrm{TPRR}(T, \tau))$ is the surface area under the curve of the TPR spectrum for the catalyst activated with hydrogen at temperature T and time τ.

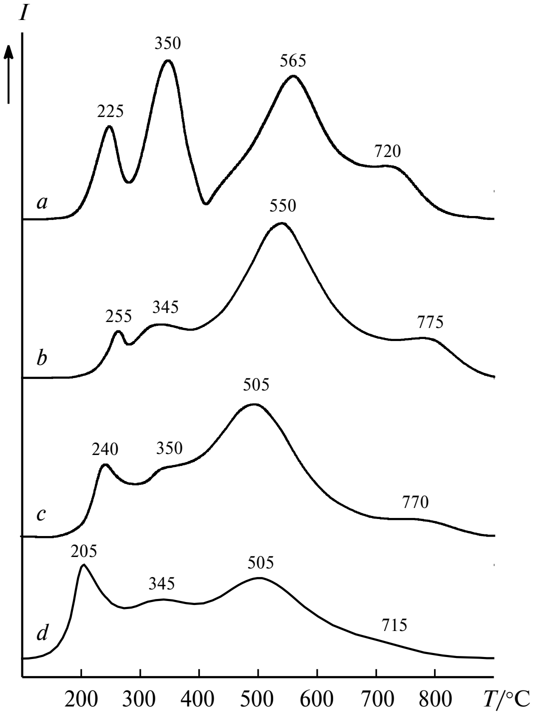


Fig. 2. Temperature-programmed reduction curves of the $Co(10\%)/ZrO_2$ catalyst calcined at 270 °C (*a*) and reduced with hydrogen at 250 °C for 1 h (*b*), at 250 °C for 24 h (*c*), and at 350 °C for 1 h (*d*).

The results of calculations of the degree of reduction of the active component under various activation conditions are given in Table 1.

The shape of the TPR spectra after the activation of the catalysts with hydrogen depends on the activation conditions (see Fig. 2, curves *b—d*). The shape of the former two peaks of hydrogen absorption and the intensities of the third and fourth peaks change as the reduction conditions (temperature or duration) become more severe (see Fig. 2). The intensity of the first peak in the TPR spectra of the pre-activated samples increases with an increase in the duration and temperature of the hydrogen treatment. Evidently, this peak cannot be attributed to the reduction of cobalt oxides Co_3O_4 and CoO and, most likely, this peak indicates the formation of new surface cobalt-containing phases during the pre-activation of the $Co(10\%)/ZrO_2$ system with hydrogen. These phases can be surface cobalt oxohydroxides,[20] which can be identified in the TPR spectra of the pre-activated samples by the first peak of hydrogen absorption

$$2\,CoO + 0.5\,H_2 \longrightarrow CoOOH + Co^0.$$

The peaks at 340—360 °C correspond to cobalt hydroxide $Co(OH)_2$ (see Ref. 17), which is an intermediate compounds formed by the reduction of the CoO(OH) phase to the Co^0 particles

$$CoOOH + 0.5\,H_2 \longrightarrow Co(OH)_2.$$

The intensity of the third reduction peak increases after the pre-activation of the $Co(10\%)/ZrO_2$ catalyst with hydrogen at 250 °C (see Fig. 2, curves *b* and *c*). This can occur due to the partial transition of unreduced bulk cobalt oxides to surface oxides. The probability of this redistribution is rather high, since the activation is carried out near the Hüttig temperature (temperature of mobility) for metallic cobalt (253 °C),[21] which leads to the agglomeration of particles of the reduced metal.

Table 1. Degree of reduction (R_{Co}), specific surface (S_{Co}), dispersity (D_{Co}), and particle size (d_{Co}) of metallic cobalt determined from the oxygen titration data under various activation conditions

τ /h	T_B /°C	$R_{Co}{}^{T,\tau}$ (%)	S_{Co} /m^2 (g of catalyst)$^{-1}$	D_{Co} (%)	d_{Co} /nm
1	250	9.3 (8.8*)	1.3	24.6	4.1
24	250	15.5 (15.2*)	1.7	19.1	5.2
1	350	34.2 (31.7*)	2.6	13.2	7.5

* According to the TPR data.

Under more severe conditions of pre-activation of the Co(10%)/ZrO_2 catalyst, the intensity of the peak corresponding to surface oxides decreases noticeably (see Fig. 2, curve *d*). According to the TPR data for the pre-calcined sample, the reduction of these oxides starts at temperatures higher than 420 °C (see Fig. 2, curve *a*); however, due to hydrogen spillover from the surface of metallic cobalt[22] formed during activation, the reduction of surface cobalt oxides on the Co(10%)/ZrO_2 catalyst becomes possible at a lower temperature (350 °C).

The presence of the Co^0 phase and an increase in its content in the catalyst also favor the reduction of cobalt in the composition of the Co—O—Zr solid solutions.[10] A nearly complete absence of this phase after reduction with hydrogen at 350 °C is due to the transition of cobalt to surface oxides CoO. This transition becomes possible at temperatures higher than the Tamman temperature[23] (the temperature at which ionic pairs of solids begin to diffuse) for cobalt oxide, *viz*., 347 °C.[24] Thus, at 350 °C cobalt oxide CoO can readily diffuse from the support lattice to the ZrO_2 surface and can more rapidly be reduced to the metal.

The degree of reduction of cobalt (R_{Co}) and its structural characteristics, namely, the surface area of metallic cobalt (S_{Co}), dispersion (D_{Co}), and diameter (d_{Co}) of Co^0 particles were determined in the experiments on the low-temperature and high-temperature adsorption of oxygen on the pre-activated Co(10%)/ZrO_2 samples. The results are presented in Table 1 along with the value of the degree of reduction of active metal determined by the TPR data of the pre-reduced catalysts. The values of R_{Co} obtained by the TPR and oxygen adsorption methods are consistent (see Table 1).

The degree of reduction of the active component increases by a factor of 1.7 as the time of the activation at 250 °C was increased from 1 to 24 h. An increase in the temperature of the preliminary hydrogen treatment to 350 °C makes it possible to increase the degree of reduction of cobalt in the Co(10%)/ZrO_2 catalyst to 32%. When the time and temperature of activation increase, the surface area of Co^0 and the crystallite size of the reduced metal increase and the value of dispersity decreases (see Table 1).

Thus, the conditions of preliminary reduction of the Co(10%)/ZrO_2 samples affect the content of Co^0 and its structural characteristics (see Table 1). The surface area, dispersion, and crystallite diameter of the active metal exert a considerable effect on the activity and selectivity of the catalyst in the formation of high-molecular-weight hydrocarbons for the classical catalysts of the Fischer—Tropsch synthesis.[25,26] No similar dependence were found for the Co/ZrO_2 system. Therefore, it was of interest to study the influence of the activation conditions on the catalytic properties of the Co(10%)/ZrO_2 samples in the synthesis of hydrocarbons from CO and H_2.

The data on the activity and selectivity at 250 °C for the Co(10%)/ZrO_2 catalysts pre-reduced with hydrogen and for the sample with no preliminary activation, as well as the compositions of liquid hydrocarbons obtained on these systems, are given in Tables 2 and 3, respectively.

The activity of the reduced samples at a synthesis temperature of 250 °C increases when the pre-activation conditions become more severe. The selectivity to methane and high-molecular-weight hydrocarbons is almost the same for all samples.

The group composition of the hydrocarbon product obtained at 250 °C is similar: normal alkanes (80—83 wt.%) and isoalkanes (15—16 wt.%) are predominantly formed with an insignificant amount of olefins (2—4 wt.%). The degree of polymerization decreases with an increase in the severity of the pre-activation conditions.

The study of the influence of the conditions for the synthesis of hydrocarbons in the presence of the Co(10%)/ZrO_2 samples on their catalytic characteristics showed that the maximum yield of hydrocarbons for all systems was 75—77 g m^{-3}. The synthesis conditions and catalytic characteristics for the systems studied are listed in Tables 4 and 5.

When the performance of the samples is compared at similar conversions of the raw materials (C_{CO} = 74—78%) and selectivity to high-molecular-weight hydrocarbons ($S_{C_{5+}}$ = 55—58%), it can be seen that the temperatures of synthesis at which these parameters achieved are different for all catalysts.

The fraction of the gasoline component in the composition of hydrocarbons obtained in the presence of the Co(10%)/ZrO_2 samples increases with softening of the activation conditions. The content of isoalkanes and olefins increases (see Table 5) due to an increase in the probability of cracking and isomerization with an increase in the temperature of the process (see Table 4). Thus, by changing the activation conditions of the Co(10%)/ZrO_2 catalytic system, one can obtain hydrocarbon products in high yields in a wide range of both fractional and group compositions.

Table 2. Conversion of CO (C_{CO}), selectivity to methane (S_{CH_4}) and hydrocarbons C_{5+} ($S_{C_{5+}}$), and yield of the liquid hydrocarbon product ($Y_{C_{5+}}$) for the Co(10%)/ZrO_2 catalysts at 250 °C, a pressure of 2 MPa, and a flow rate of 1000 h^{-1} under various activation conditions

τ/h	T_B/°C	C_{CO} (%)	$Y_{C_{5+}}$/g m^{-3}	$S_{C_{5+}}$	S_{CH_4}
				%	
—*	—	30	30	55	32
1	250	54	53	56	30
24	250	63	65	60	26
1	350	77	77	57	27

* Without activation.

Table 3. Composition of hydrocarbons C_{5+} obtained on the Co(10%)/ZrO_2 catalysts in the Fischer—Tropsch synthesis at 250 °C, a pressure of 2 MPa, and a flow rate of 1000 h^{-1}

τ/h	T_B/°C	Composition (wt.%)			Composition of paraffins (wt.%)			P*
		Olefins	*n*-Paraffins	Isoparaffins	C_5—C_{10}	C_{11}—C_{18}	C_{19+}	
—**	—	4	80	16	39	45	16	0.85
1	250	2	83	15	44	43	13	0.84
24	250	3	82	15	49	40	11	0.81
1	350	2	82	16	52	39	9	0.80

* *P* is the probability of chain growth α.

** Without activation.

The high activity observed for all Co(10%)/ZrO_2 samples and exhibited at various temperatures of the synthesis is explained by specific features of formation of the sites active in the Fischer—Tropsch synthesis.

On the samples reduced at 350 °C, the major part of cobalt exists in the metallic state and is formed during direct reduction with hydrogen.

The same levels of conversion on the Co(10%)/ZrO_2 samples reduced with hydrogen at 250 °C for 1 and 24 h were attained at higher temperatures (265 and 260 °C, respectively). Probably, in these systems the necessary amount of Co^0 and oxide components of the active sites appear only during the synthesis. The transformation of the oxide phases of cobalt into metallic cobalt at the initial steps of the synthesis occurs due to the reaction with carbon monoxide. This is confirmed by high (up to 100% in the first hours) values of selectivity to the formation of carbon dioxide on the unactivated catalysts. Cobalt oxides can be reduced under a high partial hydrogen pressure[18] in the reactor (~1.2 MPa) at temperatures higher than 200 °C corresponding to the onset of the first reduction peak in the TPR spectrum of the pre-calcined sample Co(10%)/ZrO_2 (see Fig. 2, curve *a*). The oxohydroxide phases of Co are transformed into Co^0 under the same conditions.

The action of CO on the cobalt catalysts results in the adsorption-activated increase in the dispersion of the cobalt phases,[27] which prevents crystallite sintering.[28] Since the total number of active sites of the catalyst is a function of both the dispersity of cobalt and its reducibility,[25] the Co(10%)/ZrO_2 system, which underwent no pre-activation and is characterized, hence, by the lowest degree of cobalt reduction, exhibits the minimum activity at 250 °C. On further increase in the synthesis temperature the diffusion of metallic cobalt on the catalyst surface is intensified,[29] resulting in the deep transformation of the active surface.[26] Therefore, the sample, which was not subjected to pre-activation, attains the maximum productivity only at 275 °C. Similar transformations of the solid catalyst surface accompanied by a change in the character of the active sites were observed by other researchers[30] under the Fischer—Tropsch conditions.

Under the action of the reaction conditions, the cobalt oxide compounds forming solid solutions in the Co—O—Zr system are transformed into the cobalt phase to become a fraction of the active sites. This favorably distinguishes zirconia from alumina and other classical supports of the cobalt catalysts of the Fischer—Tropsch synthesis characterized by the irreversible formation of compounds upon insertion of cobalt into the support lattice.

The results of physicochemical studies and catalytic tests of the Co(10%)/ZrO_2 system activated under conditions of varying severity make it possible to consider the mechanism of transformations of the active phase of the catalysts in the processes of reductive activation and direct synthesis of hydrocarbons from CO and H_2 (Scheme 1).

Three cobalt-containing phases can exist on the catalyst surface after the calcination of zirconia impregnated with an aqueous solution of cobalt nitrate at 270 °C for 1 h: bulk cobalt oxide Co_3O_4 distributed over the Co_3O_4 surface and a solid solution Co—O—Zr formed upon the isomorphic substitution of zirconium atoms by cobalt atoms during preparation. When the Co(10%)/ZrO_2 catalysts is activated with hydrogen at 250 °C, the bulk oxide Co_3O_4 is reduced to CoO and forms the surface oxide (see Scheme 1, steps *1* and *5*). The formation of metallic cobalt bound to the support surface is possible at this temperature due to the stepwise reduction of surface CoO through the steps of

Table 4. Conversion of CO (C_{CO}) and selectivity to methane (S_{CH_4}) and hydrocarbons C_{5+} ($S_{C_{5+}}$) for the Co(10%)/ZrO_2 catalysts in the Fischer—Tropsch synthesis at the maximum yield of high-molecular-weight hydrocarbons ($Y_{C_{5+}}$)

τ/h	T_B	T	C_{CO} (%)	$Y_{C_{5+}}$/g m^{-3}	$S_{C_{5+}}$	S_{CH_4}
	°C				%	
—*	—	275	78	77	55	26
1	250	265	74	76	58	26
24	250	260	75	75	57	24
1	350	250	77	77	57	27

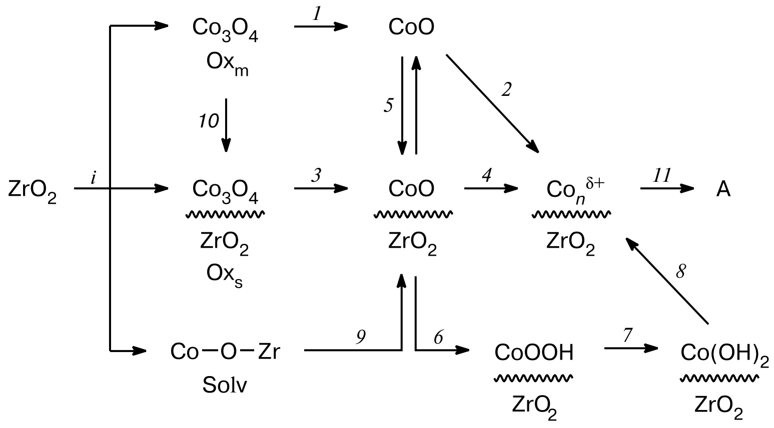
* Without activation.

Table 5. Composition of hydrocarbons C_{5+} obtained on the Co(10%)/ZrO_2 catalysts in the Fischer—Tropsch synthesis at the maximum yield of high-molecular-weight hydrocarbons

τ/h	T_B/°C	Composition (wt.%)			Composition of paraffins (wt.%)			*P*
		Olefins	*n*-Paraffins	Isoparaffins	C_5—C_{10}	C_{11}—C_{18}	C_{19+}	
—*	—	8	66	26	70	27	3	0.74
1	250	4	76	20	56	36	8	0.77
24	250	5	76	19	58	35	7	0.76
1	350	2	82	16	52	39	9	0.80

* Without activation.

Scheme 1



i. Impregnation with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$, then calcination (270 °C), 1 h.

Ox_m is bulk oxide, Ox_s is surface oxide, Solv is solid solution, and A is active site.

formation of cobalt oxohydroxide and hydroxide (steps *6*, *7*, and *8*) and it is favored by a prolonged activation. Bulk cobalt(II) oxide is reduced to an insignificant extent at 250 °C (step *2*).

The activation of the Co(10%)/ZrO_2 system at 350 °C leads to the formation of metallic cobalt due to the direct reduction of bulk (steps *1* and *2*) and surface oxides (steps *1*, *5*, and *4*) and due to the involvement of cobalt from the solid solutions (steps *9* and *4*). The formation of $Co_n^{\delta+}$ due to transformations through the steps of hydroxide formation occurs to an insignificant extent.

The initial formation of active sites of synthesis of high-molecular-weight hydrocarbons from metallic cobalt occurs under the conditions of preliminary activation (step *11*). Based on results of the catalytic experiments (see Table 4) it can be stated that the number of active sites increases with an increase in the severity of conditions of pre-activation with hydrogen.

When the synthesis of hydrocarbons from CO and H_2 is conducted under a high pressure of the reactants and at the synthesis temperatures, the bulk oxide Co_3O_4 is redistributed into the surface phase Co_3O_4 under the action of carbon monoxide at slow heating to the initial temperature of the synthesis (170 °C) (step *10*). Then the oxide is reduced to oxide CoO due to the reaction with carbon monoxide and hydrogen under elevated pressure (2 MPa) (step *3*). A further temperature increase and the presence of the reductive medium in the reactor (synthesis gas) favor the transition of CoO (step *4*) of the oxohydroxide and hydroxide phases of cobalt (steps *7* and *8*) to surface particles of metallic cobalt well dispersed on the support. This process involves hydrogen spillover with primarily formed $Co_n^{\delta+}$ and zirconia. At high conversions of the raw materials, the catalyst surface is deeply rearranged to form additional active sites of synthesis of high-molecular-weight hydrocarbons involving the $Co_n^{\delta+}$ phase and the oxide phases of cobalt[10] (step *11*).

In this work, we used the TPR, powder X-ray diffraction analysis, and oxygen adsorption methods to study specific features of the preliminary activation of the Co/ZrO_2 catalytic system with hydrogen at the process temperature (250 °C) and varying times of activation (1 and 24 h). The results obtained are compared with those acquired for the sample activated at the elevated temperature (350 °C, 1 h).

This allowed us to study the processes of reduction of various phases of cobalt and suggest the structure and composition of the active sites for the Co/ZrO_2 catalysts. Moreover, the main features of their formation during hydrogen activation under various conditions and in the process of the subsequent synthesis of hydrocarbons from CO and H_2 were outlined and the differences in the behavior of the studied catalytic systems were revealed.

References

1. A. Y. Khodakov, W. Chu, P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692.
2. W. H. Lee, C. H. Bartolomew, *J. Catal.*, 1989, **120**, 256.
3. C. R. Reuel, C. H. Bartholomew, *J. Catal.*, 1984, **85**, 78.
4. A. L. Lapidus, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1991, 2681 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.* (*Engl. Transl.*), 1991, **40**, 2335].
5. W. H. Lee, C. H. Bartholomew, *J. Catal.*, 1989, **120**, 256.
6. A. L. Lapidus, D. A. Grigor´ev, M. N. Mikhailov, A. N. Loginova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2010, 1629 [*Russ. Chem. Bull.*, *Int. Ed.*, 2010, **59**, 1657].
7. L. Shi, J. Chen, Y. Sun, *Stud. Surf. Sci. Catal.*, 2007, **167**, 97.
8. I. D. Lick, A. Carrascull, M. Ponzi, E. N. Ponzi, I. L. Botto, *Mater. Chem. Phys.*, 2005, **92**, 327.
9. J. G. Chen, Y.-H. Sun, *Stud. Surf. Sci. Catal.*, 2004, **147**, 277.
10. D. I. Enache, B. Rebours, M. Roy-Auberger, R. Revel, *J. Catal.*, 2002, **205**, 346.
11. H. Lin, C. Wang, H. Chiu, S. Chien, *Catal. Lett.*, 2003, **86**, 63.
12. G. R. Moradi, M. M. Basir, A. Taeb, A. Kiennemann, *Catal. Commun.*, 2003, **4**, 27.
13. J. Lojewska, W. Makowski, T. Tyszewski, R. Dziembaj, *Catal. Today*, 2001, **69**, 409.
14. S. Kittiruangrayab, T. Burakorn, B. Jongsomjit, P. Praserthdam, *Catal. Lett.*, 2008, **124**, 376.
15. D. I. Enache, M. Roy-Auberger, R. Revel, *Appl. Catal. A: General*, 2004, **268**, 51.
16. T. Yamaguchi, *Catal. Today*, 1994, **20**, 199.
17. L. A. Bruce, G. J. Hope, J. F. Mathews, *Appl. Catal.*, 1983, **8**, 349.
18. P. A. Chernavskii, A. Y. Khodakov, G. V. Pankina, J.-S. Girardon, E. Quinet, *Appl. Catal.*, 2006, **306**, 108.
19. A. Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson, P. Chaumette, *J. Catal.*, 1997, **168**, 16.
20. J. van de Loosdrecht, S. Barradas, E. A. Caricato, N. G. Ngwenya, P. S. Nkwanyana, M. A. S. Rawat, B. H. Sigwebela, P. J. van Berge, J. L. Visagie, *Top. Catal.*, 2003, **26**, 121.
21. A. Moulijn, A. E. van Diepen, F. Kapteijn, *Appl. Catal. A*, 2001, **212**, 3.
22. G. Jacobs, Y. Ji, B. H. Davis, D. Cronauer, A. J. Kropf, C. L. Marshall, *Appl. Catal. A*, 2007, **333**, 177.
23. J. Thewlis, *Encyclopedic Dictionary of Physics*, 1962, 171.
24. L. Zhang, L. Dong, W. Yu, L. Liu, Y. Deng, B. Liu, H. Wan, F. Gao, K. Sun, L. Dong, *J. Colloid Interface Sci.*, 2011, **355**, 464.
25. J.-S. Girardon, E. Quinet, A. Griboval-Constant, P. A. Chernavskii, L. Gengembre, A. Y. Khodakov, *J. Catal.*, 2007, **248**, 143.
26. A. Y. Khodakov, R. Bechara, A. Griboval-Constant, *Appl. Catal. A*, 2003, **254**, 273.
27. V. A. de la Pen̆a O´Shea, J. M. Campos-Martýn, J. L. G. Fierro, *Catal. Commun.*, 2004, **5**, 635.
28. B. Jongsomjit, J. G. Goodwin, Jr., *Catal. Today*, 2002, **77**, 191.
29. N. E. Tsakoumis, M. Ronning, O. Borg, E. Rytter, A. Holmen, *Catal. Today*, 2010, **154**, 162
30. H. Schulz, Z. Nie, F. Ousmanov, *Catal. Today*, 2002, **71**, 351.

Received July 21, 2011