Full Articles

Formation of the Co/ZrO_2 catalyst active phase in the Fischer—Tropsch synthesis

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Thermoprogrammed reduction and X-ray powder diffraction were used to study the phase composition and specific features of the activation process of the Co/ZrO_2 catalytic system. Results of the physico-chemical studies were compared with the data on activity and selectivity of catalysts in the Fischer—Tropsch synthesis. Reducing activation of the Co/ZrO_2 catalyst with the syn-gas can be performed directly during the Fischer—Tropsch synthesis, avoiding the high-temperature step of reduction with hydrogen. The Co/ZrO_2 catalytic system can be used for the development of catalysts for the Fischer—Tropsch synthesis, which do not require a separate step of the high-temperature reduction with hydrogen.

Key words: cobalt catalyst, the Fischer—Tropsch synthesis, zirconia, activation of catalyst.

Classic cobalt Fischer—Tropsch catalysts based on alumina, silica, and alumosilicates possess high activity and selectivity.[1,2] One of the principal steps in the formation of active phase of these catalysts is the activation in reducing atmosphere, necessary for the formation of reduced particles of cobalt on the catalyst surface.[3] Recent works[4—7] showed that when a precursor of the active component is deposited on a support, formation of difficult-to-reduce mixed oxides (spinel structures)[8,9] occurs, that leads to the transformation of considerable amount of active component into the catalytically inert state. Since formation of the spinel structures is directly related to the active component—support interaction, more recently attention of researches was directed on the development of new catalytic systems with lower strength of the metal—support interaction. In particular, the Co/ZrO_2 system belongs to such systems (see Ref. 10).

In the present work, we studied conditions for the formation of active phase in the Co/ZrO_2 catalytic system and their influence on activity and selectivity of the Fischer—Tropsch catalyst.

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Experimental

Support was prepared from zirconia, obtained by calcination of $ZrO(NO_3)_2 \cdot 6H_2O$ (Aldrich) for 4 h at 400 and 800 °C (the ZR1 and ZR2 supports, respectively). Powdered zirconia containing 10% boehmite, was formed into the cylinder-shaped pellets 2.5 mm in diameter and 4—6 mm in length. The pellets obtained were calcined for 4 h at 500 °C. Cobalt was deposited into the catalyst by impregnation of the support with aqueous solution of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (10 wt.%). After the impregnation, the catalyst was calcined for 1 h at 400 °C.

X-ray diffraction analysis was performed on a DRON-3 diffractometer at the scanning rate of 0.5 deg min^{-1}, using CuKα-irradiation and cerium oxide as the internal standard (10 wt.% with respect to the weight of the sample). The mean diameter of the crystallites in the samples of calcined catalyst was determined from the Debye—Scherrer equation.[11]

Thermoprogrammed reduction (TPR) of catalysts (250 mg) was performed on a AutoChem II 2920 instrument (Micromeritics) in the flow (10 mL min^{-1}) of the 5%H_2 + 95%Ar gas mixture. The linear elevation of temperature was carried out from 50 to 750 °C at the rate 10 deg min^{-1}.

The adsorption/desorption isotherm of nitrogen was measured using a ASAP 2010 instrument (Micromeritics). The surface area of the samples was calculated using the Brunauer—Emmett—Teller (BET) equation.[12] The size distribution of pores and their average diameter were determined using the Barrett—Joyner—Halenda method.[13]

Microcatalytic experiments were performed in a fixed-bed steel reactor (13 mm in internal diameter), P = 2 MPa, $H_2 : CO : N_2$ = 63 : 31.5 : 5.5 (vol.%). Catalysts reduced with hydrogen and catalysts without preliminary reducing treatment were activated in the flow of syn-gas (the volume rate was 1000 h^{-1}). A catalyst was heated to 170 °C at the rate 2 deg min^{-1} and kept at this temperature until stable indices on conversion of carbon monoxide and selectivity to liquid hydrocarbons and methane were reached. Then, the temperature was step-wise elevated by 10 °C until degree of transformation of carbon monoxide reached 50—60%. After that, the temperature was step-wise elevated by 5 °C until conversion of carbon monoxide reached 70—80%.

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

Results and Discussion

The X-ray patterns of the ZR1 and ZR2 supports are shown in Fig. 1. As it is seen from the Figure, the calcination of zirconium oxonitrate leads to the formation of a mixture of two crystalline phases of zirconia, *viz.*, the tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2). If the calcination temperature is increased, the content of the monoclinic phase increases, whereas the content of the tetragonal phase decreases. The ZR1 support calcined at 400 °C contains about 80% tetragonal and 20% monoclinic phases, whereas in the case of the ZR2 support subjected to the thermal treatment at 800 °C, contribution of the monoclinic phase increases to 95%. The study of the formation of zirconia phase from zirconium oxyhydroxide[14] showed that the formation of the tetragonal phase is observed at the temperatures higher 550 °C, whereas the monoclinic phase appears only at 1200 °C. To sum up, the use of zirconium oxonitrate allows us to obtain the crystalline phases of zirconia at lower calcination temperature.

Physico-chemical properties of the ZrO_2 support samples are given in Table 1. It is seen that on going from the tetragonal phase to the monoclinic, the size of crystallites increases, whereas the support specific surface and the volume of pores decrease. The significant increase in the size of crystallites upon increase in contribution of the monoclinic phase has been noted earlier during study of the reaction of cobalt with the surface of zirconia by electron microscopy and X-ray diffraction.[10]

The TPR curves of the 10%Co/ZrO_2 catalysts are shown in Fig. 2. The TPR spectrum of the 10%Co/ZR2 catalyst, prepared based on the monoclinic modification of zirconia, exhibits three peaks at the temperatures 240, 310, and 510 °C. The first two peaks correspond to the reduction of Co_3O_4 to CoO, whereas the third peak is attributed to the reduction of CoO to metallic cobalt.[4,15] Cobalt oxide Co_3O_4 on the 10%Co/ZR2 catalyst is reduced in two steps. Apparently, it is due to the fact that crystallites of Co_3O_4 of different sizes are present on its surface, since the reduction temperature of cobalt(II, III) oxide strongly depends on the size of its particles.[16] It is

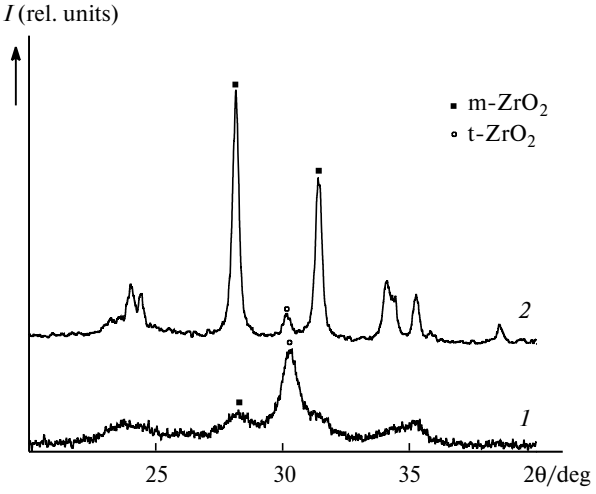

Fig. 1. X-ray patterns of the ZR1 (*1*) and ZR2 (*2*) supports.

Table 1. Physico-chemical properties of the ZrO_2 support samples

Support	$S/m^2\ g^{-1}$	$V_p/cm^3\ g^{-1}$	D_p^{av}/nm	d_{ZrO_2}/nm
ZR1	61.9	0.19	10.1	11.5
ZR2	32.1	0.13	14.2	41.0

Note. S is the surface square, V_p is the volume of pores, D_p^{av} is the average diameter of pores, d_{ZrO_2} is the average size of ZrO_2 crystallites.

Table 2. Degree of reduction of the 10%Co/ZrO_2 catalysts at different temperatures

T/°C	RD_{Co} (%)	
	10%Co/ZR1	10%Co/ZR2
350	17.3	28.1
500	56.4	65.6

known[17] that in the cobalt systems characterized by a strong metal—support interaction (for example, alumina), at increased temperatures the reduction of cobalt in the large Co_3O_4 crystallites is favored in the first place, whereas small crystallites are reduced at higher temperatures. Since zirconia is characterized by a weak interaction with active component, the Co_3O_4 crystallites of smaller size are reduced[10] in the Co/ZrO_2 system in the low-temperature region (240 °C), whereas large particles are reduced at higher temperature (310 °C).

Two broad peaks at the temperatures 300—400 (the maximum 360 °C) and 400—600 °C (the maximum 510 °C) are seen on the TPR curve of the 10%Co/ZR1 catalyst based on the tetragonal modification of zirconia. The first peak is related to the reduction of cobalt oxide Co_3O_4 to CoO and it is displaced to higher temperatures by 50 °C as compared to that of the monoclinic modification of the catalyst. The second peak corresponds to the reduction of CoO to metallic cobalt Co^0 (see Refs 15 and 16). In the TPR spectra (see Fig. 2), no high-temperature (>600 °C) peaks of reduction are observed, that indicates the absence of difficult-to-reduce cobalt zirconates on the catalyst surface.[18]

Table 2 contains the data on the degree of reduction of cobalt (RD_{Co}) at different temperatures for the 10%Co/ZR1 and 10%Co/ZR2 catalysts, which was evaluated as a ratio of the area under the TPR curve limited by the corresponding temperature to the total area. The value of RD_{Co} obtained at 350 °C for the 10%Co/ZR2 (28%) catalyst indicates that almost all the Co_3O_4 is reduced to CoO by this temperature, whereas metallic cobalt is present in small amounts. At the temperature 500 °C, the degree of reduction reaches 66% and the most part of cobalt is in the metallic state. For the 10%Co/ZR1 catalyst, the degree of reduction at temperatures 350 and 500 °C is lower than for the 10%Co/ZR2 catalyst.

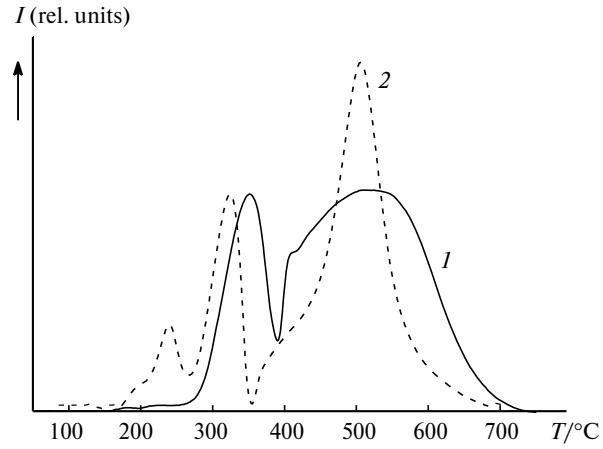

Fig. 2. The TPR curves of the 10%Co/ZR1 (*1*) and 10%Co/ZR2 (*2*) catalysts.

The X-ray patterns of 10%Co/ZR1 and 10%Co/ZR2 catalysts calcined at 400 °C and reduced at 350 °C are shown in Fig. 3. The X-ray patterns of unreduced samples contain lines related to the oxide phase Co_3O_4. Mean size of the Co_3O_4 crystallites, calculated using the Debye—Scherrer equation, is about 200 Å. Upon reduction of the catalysts at 350 °C, the lines of the crystalline Co_3O_4 phase disappear, obviously, as a result of the fact that the spinel phase of Co_3O_4 is completely reduced with the formation of the amorphous to X-rays phase of CoO. It is known from the literature[19] that for the Co_3O_4 phase to be reduced on the supports of the Al_2O_3 and SiO_2 type, the temperatures not lower than 450 °C are required. The XRD data for the 10%Co/ZrO_2 catalysts allow us to draw a conclusion that the absence of the strong metal—support interaction promotes decrease in the reduction temperature of the catalyst.

Analysis of Fig. 2 shows that the reduction process of cobalt on the 10%Co/ZrO_2 catalysts begins at temperatures 200—300 °C, which is close to the temperatures of the Fischer—Tropsch synthesis. A decrease in the initial temperature of reduction of cobalt on these catalysts is also evidenced by the X-ray diffraction data, according to which the Co_3O_4 phase completely disappears in the samples treated with hydrogen at 350 °C. Therefore, it was of interest to find whether the 10%Co/ZrO_2 catalysts, that were not subjected to a special step of reducing treatment, as well as the catalysts reduced at decreased temperature of 350 °C, possess activity in the Fischer—Tropsch synthesis. The data on activity and selectivity of the 10%Co/ZR1 and 10%Co/ZR2 catalysts, preliminary reduced with hydrogen at 350 °C (T_r) (the volume rate 3000 h^{-1}, 1 h), and the 10%Co/ZR1 catalyst treated with the syn-gas only during the reaction are given in Tables 3 and 4. It is seen from the Tables that 10%Co/ZR1 and 10%Co/ZR2 samples having different modification of

Table 3. Activity and selectivity of the 10%Co/ZrO_2 catalysts in the Fischer—Tropsch synthesis at the pressure 20 atm and volume rate 1000 h^{-1}

Catalyst	T_r /°C	T /°C	Conversion CO (%)	$Y_{C_{5+}}$ /g m^{-3}	$S_{C_{5+}}$ (%)	S_{CH_4} (%)
10%Co/ZR2	350	250	78	76	54	28
10%Co/ZR1	350	250	78	80	57	27
10%Co/ZR1	—	275	78	81	55	26

Note. T_r is the temperature of preliminary reduction of catalysts with hydrogen, T is the temperature of reaction, $Y_{C_{5+}}$ is the yield of hydrocarbons, $S_{C_{5+}}$ is the selectivity on liquid hydrocarbons, S_{CH_4} is the selectivity on CH_4.

zirconia support and reduced at 350 °C, show no considerable differences. The maximum yield of C_{5+} hydrocarbons is reached at the temperature about 250 °C and at 78% conversion of CO. The fractional composition of liquid hydrocarbons (see Table 4) obtained on these catalysts is also virtually the same and mainly consists from the fractions C_5—C_{10} (50%) and C_{11}—C_{18} (40%), that corresponds to the gasoline and diesel fractions.

Since no differences between the 10%Co/ZrO_2 catalysts, differing in the phase composition of zirconia, were found, the study of activation of the catalyst with the syngas at temperatures of the Fischer—Tropsch synthesis was performed for the sample of 10%Co/ZR1. As it is seen from the data in Table 3, the 10%Co/ZR1 catalyst, activated with the syn-gas without preliminary treatment with hydrogen, showed high activity in the Fischer—Tropsch synthesis and was not inferior in the yield of hydrocarbons C_{5+} to the catalysts undergone the special reducing treatment. This catalyst in its activity and selectivity is comparable to the classic catalysts of the Fischer—Tropsch synthesis.[20,21] In the products of the synthesis obtained on this catalyst, the content of the gasoline fraction increases to 70%, with the content of normal alkanes being considerably decreased. At the same time, the content of olefins and iso-alkanes in the reaction products increases. Such changes of the product composition, obviously, are due to the increase in the optimum temperature of the process by 25 °C.

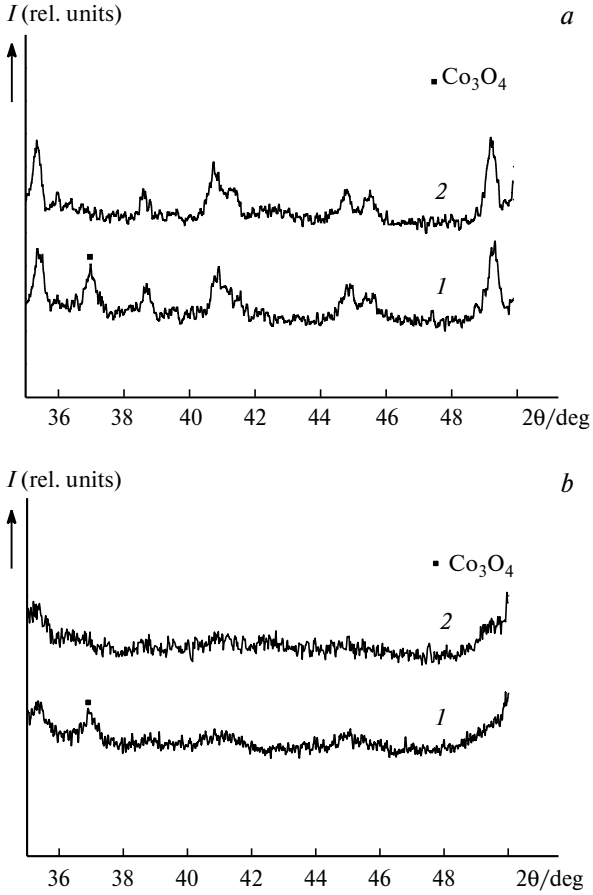

Fig. 3. X-ray patterns of the 10%Co/ZR2 (*a*) and 10%Co/ZR1 (*b*) catalysts, calcined at 400 °C (*1*) and reduced at 350 °C (*2*).

High activity of the catalyst that was not subjected to reducing treatment with hydrogen described above is apparently explained by the fact that on the surface of zirconia, the formation of reduced particles of cobalt is possible in two ways: as a result of action of hydrogen during high-temperature reduction of the catalyst and under conditions of the synthesis of hydrocarbons from CO and H_2 (see Ref. 22). On the preliminary reduced catalyst, cobalt is partially present in the form of metal and the number of active centers of metallic cobalt increases with the temperature of reduction. On the sample unreduced with

Table 4. Composition of C_{5+} hydrocarbons, obtained on the 10%Co/ZrO_2 catalysts in the Fischer—Tropsch synthesis at the pressure 20 atm and volume rate 1000 h^{-1}

Catalyst	T_r/°C	Composition (wt.%)			Composition of paraffins (wt.%)			P
		Olefins	H-paraffins	Isoparaffins	C_5—C_{10}	C_{11}—C_{18}	C_{19+}	
10%Co/ZR2	350	2	81	17	52	39	9	0.80
10%Co/ZR1	350	2	82	16	51	39	10	0.81
10%Co/ZR1	—	8	66	26	70	27	3	0.74

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

hydrogen, Co^0 begins to appear only in the process of synthesis and its amount, necessary for the conversion of CO required to be achieved, is formed at higher temperatures of the process.

The results obtained can be used in the development of new promising catalysts for the Fischer—Tropsch synthesis, which require no special step of the high-temperature reduction with hydrogen.

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