Effect of epitaxial growth on the formation of the cobalt catalysts of the Fischer—Tropsch synthesis*

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Mixed oxides $Co_xAl_yO_4$ with different Al/Co ratios applied as supports for the catalysts of the Fischer—Tropsch synthesis were prepared using the solid-state chemical reaction. The $Co_xAl_yO_4$ supports were prepared by modifying gibbsite with various cobalt salts (acetate, nitrate, and basic carbonate). The use of basic cobalt carbonate gives the $Co(20\%)/Co_xAl_yO_4$ catalyst, which provides an increased yield of hydrocarbons C_{5+} and a decreased methane content compared to the impregnation catalyst $Co(30\%)/Al_2O_3$. The introduction of small amounts of rhenium additives makes it possible to enhance the yield of hydrocarbons C_{5+} (179 g m^{-3}) and also to increase the selectivity with respect to the C_5—C_{18} fraction. The introduction of basic cobalt carbonate into the support, most likely, creates favorable conditions for the epitaxial growth of the precursor of the active phase.

Key words: Co/Al_2O_3 catalyst, Fischer—Tropsch synthesis, epitaxial growth.

The Fischer—Tropsch synthesis (FTS) is one of few processes for the preparation of motor fuels from non-petroleum raw materials.[1,2] Great attention was given to the modification of the classical Co/Al_2O_3 catalysts aimed at controlled enhancement of activity and selectivity.[3,4] The authors[5—9] attempted to increase the activity and selectivity of the catalysts only by the introduction of various promoters. The chemical modification of the support is studied much more poorly. At the same time, the studies[10—14] of the Co/Al_2O_3 system showed a strong metal—support interaction. It has recently[15] been found that the electronic state of a metallic component is noticeably affected by interactions of the following types: metal—surface hydroxyl groups, metal—basic sites, and metal—Lewis acid sites. In its turn, the catalytic activity depends substantially on the contribution of these interactions. A promising approach for controlling the strength of the metal—support interaction is a choice of an optimum ratio of the structural parameters of the active component and support (epitaxy).[16] The epitaxy effect on the behavior of the FTS catalysts has not virtually been studied to date.[17] The Co_3O_4 phase with a lattice constant of 8.083—8.170 Å is formed on the support surface upon the preparation of the Co/Al_2O_3 catalyst. Since the lattice parameter of γ-Al_2O_3 (7.905 Å) is lower than that for Co_3O_4, it can be assumed that the supports with a larger unit cell volume, in particular, mixed oxides $Co_xAl_yO_4$ (lattice parameter 8.072—8.109 Å), meet better the solid-state epitaxy mode. Therefore, it was of interest to reveal a possibility of improving the catalytic properties of the Co/Al_2O_3 FTS catalysts when the $Co_xAl_yO_4$ mixed oxides are used as supports. In this work, we studied the behavior of the cobalt FTS catalysts based on the $Co_xAl_yO_4$ mixed oxides.

Experimental

The $Co(20\%)/Co_xAl_yO_4$ catalysts based on $Co_xAl_yO_4$ mixed oxides were studied.[18] The $Co_xAl_yO_4$ supports were prepared by the solid-state reaction using the calcination of a mechanical mixture of a cobalt salt (nitrate, acetate, or basic carbonate) with gibbsite at 650 °C for 10 h. The $Co(20\%)/Co_xAl_yO_4$ catalysts were prepared by the double impregnation of the $Co_xAl_yO_4$ support with an aqueous solution of cobalt nitrate, introducing 10% Co every treatment. After each impregnation, the sample was calcined for 1 h in an air flow at 400 °C. In addition, the $Co(20\%)/Co_xAl_yO_4$ catalyst based on gibbsite and basic cobalt carbonate was modified by the addition of Pd, Ru, and Re. The promoters were introduced by catalyst impregnation with aqueous solutions of the corresponding salts. The $Co(30\%)/Al_2O_3$ sample was used as the reference catalyst. The support for this catalyst was prepared by gibbsite calcination in air in a muffle furnace at 650 °C for 10 h and then cobalt (30 wt.%) was introduced by impregnation with an aqueous solution of cobalt ni-

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trate (in three steps). After each impregnation step, the sample was dried in a water bath and calcined for 1 h in an air flow at 400 °C.

Hydrocarbons were synthesized from CO and H_2 in a flow-type catalytic reactor under atmospheric pressure. A catalyst powder was pelletted and crushed, and a fraction of 100—250 μm was taken for the catalytic experiment. The catalyst (20 cm^3) was loaded in a quartz reactor with an internal diameter of 20 mm. Before loading the catalyst was mixed with quartz in the volume ratio catalyst : quartz = 1 : 3. Before synthesis, the samples were reduced for 1 h in a hydrogen flow (99.999%, flow rate 3000 h^{-1}) at 450 °C. Then the catalysts were treated in a synthesis gas flow (flow rate 100 h^{-1}, volume ratio $H_2 : CO : N_2$ = 63 : 32 : 5), increasing the temperature from 160 to 210 °C by 10 °C at an interval of 5 h. The data on the catalytic activity presented below were obtained at 200 °C. At this temperature the optimum yield/selectivity ratios for hydrocarbons C_{5+} were recorded. Liquid hydrocarbons were trapped and analyzed by GLC (flame-ionization detector, He as carrier gas, column: DB Petra 0.5 phase, l = 50 m, d = 0.2 mm, T = 50—250 °C, heating rate 3 deg min^{-1}). The starting mixture and gaseous products of the synthesis were analyzed by gas adsorption chromatography (katharometer as detector, He as carrier gas, column *1* (CO and CH_4): CaA phase, l = 3 m, d = 3 mm, T = 80 °C; column *2*: HayeSep phase, l = 3 m, d = 3 mm, T = 80—200 °C, heating rate 8 deg min^{-1}). X-ray diffraction analysis was carried out with a DRON-2 diffractometer (CuKα radiation, scanning rate of 0.5 deg min^{-1}). The internal standard (CeO_2) in an amount of 10 wt.% was introduced into the samples to refine the unit cell constants.

Results and Discussion

The main parameters determining the productivity of the catalysts of the Fischer—Tropsch synthesis are the CO conversion, yield of hydrocarbons C_{5+}, and selectivity with respect to hydrocarbons C_{5+}. Taking into account that the FTS includes many different steps, the formation of the target products is inevitably accompanied by the appearance of by-products, mainly methane and CO_2.[18] Therefore, the most promising catalysts are characterized by the high CO conversion and also by the low yield of by-products, *viz.*, methane and CO_2.

The X-ray diffraction patterns of gibbsite calcined at 650 °C exhibits several diffuse reflections, whose position and intensity correspond to the γ-Al_2O_3 crystalline phase with an average crystallite size of ~50 Å and a lattice parameter of 7.910 Å. The X-ray diffraction patterns of the supports obtained by the solid-state synthesis contain six reflections characteristic of the crystalline $Co_xAl_yO_4$ mixed oxide along with the lines of γ-Al_2O_3 (Fig. 1). The absence of noticeable peak broadening indicates that the mixed oxide is presented by large crystals with sizes more than 500 Å. Table 1 presents the calculated lattice constants (a_0) of the supports prepared by dry mixing of gibbsite with the following cobalt compounds: basic carbonate, nitrate, and acetate. The lattice constant ranges

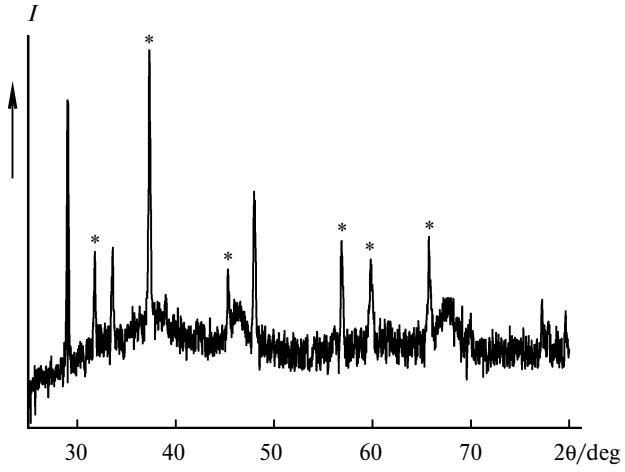

Fig. 1. X-ray diffraction pattern of the support prepared from gibbsite and basic cobalt carbonate (reflections of the $Co_xAl_yO_4$ mixed oxide are marked with asterisk).

from 8.025 Å for cobalt nitrate to 8.103 Å for basic cobalt carbonate. It is seen that the nature of the precursor substantially affects the structural features of the mixed oxide phase. The comparison of the a_0 values for the supports shows that the modification of alumina with basic carbonate results in the formation of the phase with the lattice parameter closest to the a_0 value characteristic of Co_3O_4. The unit cell volume decreases consequently with an increase in the Al/Co ratio from 3 to 9.

Let us consider how the nature of the starting cobalt compound affects the activity and selectivity of the FTS catalysts based on the modified supports. Selected parameters of the process obtained for the CO conversion 70% and temperature 200 °C are given in Table 2. These data show that, as compared to the Co(30%)/Al_2O_3 catalyst, the introduction of cobalt into the support substantially increases the yield of hydrocarbons C_{5+} and selectivity with respect to these hydrocarbons. In addition, the contribution of the fraction C_{19+} (~22%) and a decrease in the content of by-products are observed. The highest yield

Table 1. Lattice constants of the supports obtained by the solid-state synthesis

Compound	Al/Co (mol.)	a_0/Å
Co_3O_4	–	8.083—8.170
γ-Al_2O_3	–	7.910
$Co_xAl_yO_4$ (gibbsite + basic carbonate)	3	8.103
	6	8.091
	9	8.078
$Co_xAl_yO_4$ (gibbsite + nitrate)	6	8.025
$Co_xAl_yO_4$ (gibbsite + acetate)	6	8.043

Table 2. Selected parameters of the FTS process at 200 °C and a CO conversion of 70%

Initial compound	Yield/g m^{-3}			Selectivity (%)		Composition of products (wt.%)		
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5—C_{10}	C_{11}—C_{18}	C_{19+}
Basic carbonate	6	130	14	4	90	15	52	33
Acetate	11	110	39	9	76	15	41	44
Nitrate	8	109	29	7	76	20	50	30
$Co(30\%)/Al_2O_3$	15	105	13	13	72	33	56	11

of hydrocarbons C_{5+} was obtained when basic cobalt carbonate was used as a modifying additive.

The X-ray diffraction patterns of the $Co(30\%)/Al_2O_3$ and $Co(20\%)/Co_xAl_yO_4$ catalysts are shown in Fig. 2. It is seen that the catalyst based on the mixed oxide contains a considerable amount of the Co_3O_4 crystalline phase. At the same time, γ-Al_2O_3 is the major crystalline phase in the catalyst based on alumina, and Co_3O_4 exists mainly in the state amorphous to X-rays. As shown by the data in Table 1, the support obtained from basic cobalt carbonate most perfectly meets the epitaxial growth mode of the Co_3O_4 crystallites, because the a_0 values for Co_3O_4 and $Co_xAl_yO_4$ are rather close. The space groups for Co_3O_4, γ-Al_2O_3, and $Co_xAl_yO_4$ are the same (*Fd*3*m*). It is known that the crystallites grow on the support faces only at minor differences in the lattice parameters of the support and growing phase. In addition to the ratio of the lattice parameters, the energy of interaction of the support and precipitating crystal affects the epitaxial growth mechanism. According to the Stransky—Krastanov mechanism, two-dimensional surface phases appear in the initial condensation step, and then three-dimensional crystals are formed. The presence of a considerable amount of the Co_3O_4 crystalline phase on the surface of the $Co_xAl_yO_4$ mixed oxide agrees, most likely, with the growth mechanism. It can be assumed that the epitaxy mode favoring a stronger active component—support interaction occurs in this case. Probably, the cobalt oxide crystallites are rather easily reduced during catalyst treatment, retaining as finely dispersed particles, which prevents sintering processes. When γ-Al_2O_3 is used as a support, dense, multilayer weakly structured coatings appear, most likely, on the surface of the catalyst precursor. These coatings are more prone to sintering than the three-dimensional crystallites in the catalyst based on the mixed oxide. This assumption is favored by the catalytic data (see Table 2). The best FTS parameters were achieved in the presence of the $Co(20\%)/Co_xAl_yO_4$ catalyst based on basic cobalt carbonate, whose preparation was carried out under the conditions most favorable for epitaxial growth. The $Co(20\%)/Co_xAl_yO_4$ catalysts based on the supports modified by cobalt acetate and nitrate are inferior to the catalyst based on carbonate in activity but superior to the $Co(30\%)/Al_2O_3$ catalyst. It should be mentioned that all the $Co(20\%)/Co_xAl_yO_4$ samples are characterized by decreased methane formation.

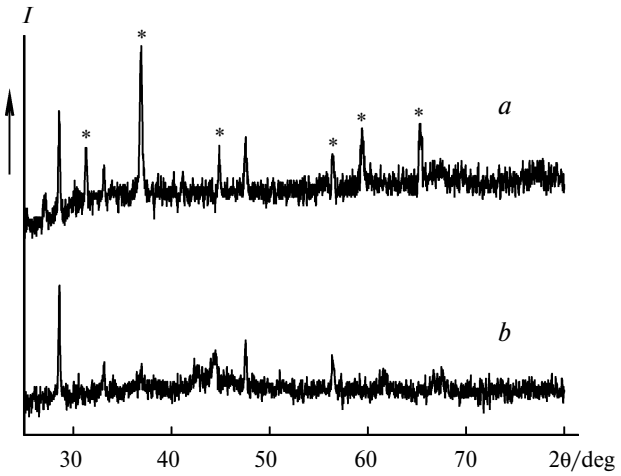

Fig. 2. X-ray diffraction patterns of the samples prepared using the support of the mixed oxide (*a*) and gibbsite (*b*) (reflections of the $Co_xAl_yO_4$ mixed oxide are marked with asterisk).

The solid-state synthesis provides mixed oxides in which the Al/Co ratio varies in a wide range. Since the best parameters of the FTS process were achieved on the catalyst made in the presence of basic cobalt carbonate, we prepared the catalysts with the Al/Co ratio (mol.) in the support equal to 3, 6, and 9. The results of studying the catalytic activity of these samples are given in Table 3. According to these data, the highest yield of hydrocarbons C_{5+} is observed on the catalyst with the ratio Al/Co = 6. An increase or decrease in this ratio results in the deviation of the a_0 value from the optimum parameter favorable for solid-state epitaxy (see Table 1) and, therefore, deteriorates the main FTS parameters (Fig. 3).

The introduction of minor amounts of the VIIIB group metals as modifying additives is a method for controlling the change in the catalytic activity of the FTS catalysts. The catalytic data obtained for the $Co(20\%)/Co_xAl_yO_4$ catalyst promoted by Pd, Ru, and Re are given in Table 4. The introduction of ruthenium and rhenium increases the yield of hydrocarbons C_{5+}, whereas the yield of the C_{5+} fraction decreases considerably in the presence of palladium. In addition, the introduction of palladium and ruthenium significantly decreases the selectivity with re-

Table 3. Selected parameters of the FTS process at 200 °C and a CO conversion of 70%

Al/Co (mol.)	Yield/g m^{-3}			Selectivity (%)		Composition of products (wt.%)		
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5—C_{10}	C_{11}—C_{18}	C_{19+}
3 (38%)	9	119	18	8	82	16	71	13
6 (32%)	6	130	14	4	90	15	52	33
9 (29%)	10	114	27	9	78	17	76	7

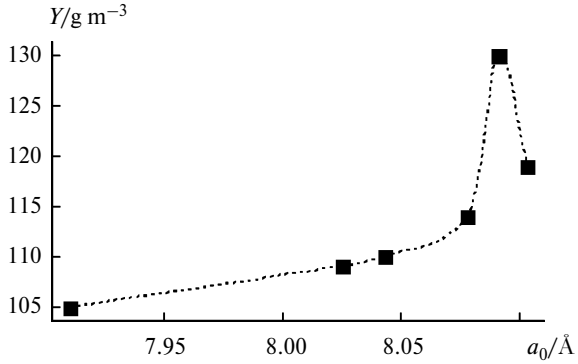

Fig. 3. The yield of liquid hydrocarbons C_{5+} (Y) at different lattice parameters of the support (a_0).

spect to hydrocarbons C_{5+} from 90 to 76 and 84%, respectively. The data in Table 4 clearly show that the promoters appreciably increase the contribution of the C_5—C_{18} fraction and substantially decrease the contribution of the C_{19+} fraction.

Thus, rhenium is the most efficient promoting additive. In the presence of rhenium, the yield of hydrocarbons C_{5+} and the contribution of the gasoline and kerosene fraction increase. Therefore, it was of interest to reveal how the rhenium content affects the activity and selectivity of the Co(20%)—Re/$Co_xAl_yO_4$ catalyst. According to the data in Table 5, the catalytic behavior of the system changes slightly with an increase in the rhenium concentration in the Co(20%)—Re/$Co_xAl_yO_4$ catalyst from 0.1 to 0.5%. The introduction of only 0.1% rhenium substantially increases the yield of hydrocarbons C_{5+} and selectivity with respect to the C_5—C_{18} fraction. The highest yield of hydrocarbons C_{5+} (170 g m^{-3}) was obtained for a rhenium concentration of 0.3%. The selectivity with respect to hydrocarbons C_{5+} decreases appreciably (to 81%) with the further increase in the Re concentration (>0.5%). It should be mentioned that all the Co(20%)—Re/$Co_xAl_yO_4$ samples were characterized by a reduced content of the major by-product methane. The selectivity with respect to methane was only 4—8% (see Table 5).

Thus, the study of active phase formation in the Co(20%)/$Co_xAl_yO_4$ FTS catalysts showed that the introduction of cobalt from basic carbonate into the support creates favorable conditions for solid-state epitaxy. Thus prepared catalysts are characterized by an enhanced yield of hydrocarbons C_{5+} and decreased methane formation. Rhenium is the most efficient promoter for these cata-

Table 4. Selected parameters of the FTS process at 200 °C and a CO conversion of 70% using different promoters

Promoter	Yield/g m^{-3}			Selectivity (%)		Composition of products (wt.%)		
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5—C_{10}	C_{11}—C_{18}	C_{19+}
In the absence of promoter	6	130	14	4	90	15	52	33
Pd (0.5%)	16	111	27	12	76	29	63	8
Ru (0.5%)	11	123	19	9	84	39	54	7
Re (0.5%)	5	132	22	4	90	24	68	8
Re(0.5%)—Co(30%)/Al_2O_3	11	120	19	9	82	20	54	26

Table 5. Selected parameters of the FTS process at 200 °C, 90% CO conversion, and different Re contents

Content of Re (wt.%)	Yield/g m^{-3}			Selectivity (%)		Composition of products (wt.%)		
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5—C_{10}	C_{11}—C_{18}	C_{19+}
0.1	8	165	43	5	88	20	68	12
0.3	7	170	40	4	90	27	68	5
0.5	7	167	40	5	88	24	68	8
0.7	12	152	61	8	81	36	62	2

lysts. The Co(20%)—Re(0.3%)/$Co_xAl_yO_4$ catalytic system differs favorably from the classical FTS cobalt catalysts in the increased yield of hydrocarbons C_{5+} and selectivity with respect to these products, as well as the low selectivity with respect to methane (major by-product of the FTS).

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