

# Formation of a Supported Cobalt Catalyst for the Synthesis of Carbon Nanofibers on Aluminum Oxide

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**Abstract**—Comparative studies of the effect of the physicochemical characteristics of a support (aluminum oxide) on the formation of a supported Co catalyst and its activity in the pyrolysis of alkanes (propane–butane) were performed. The effect of the crystalline modification of alumina on the yield of catalytic filamentous carbon (CFC) ((g CFC)/(g Co)) was studied. The surface morphologies of Co-containing catalysts and synthesized carbon deposits were studied by scanning electron microscopy. It was found that carbon deposits with a well-defined nanofiber structure were synthesized by the pyrolysis of a propane–butane mixture in the presence of hydrogen at 600°C on supported Co catalysts prepared by homogeneous precipitation on macroporous corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ). The yield of CFC was no higher than 4 (g CFC)/(g Co). On the Co catalyst prepared by homogeneous precipitation on mesoporous  $\text{Al}_2\text{O}_3$ , the intense carbonization of the initial support; the formation of cobalt aluminates; and, as a consequence, the deactivation of  $\text{Co}^0$  as a catalyst of FC synthesis occurred. The dependence of the yield of CFC on the preheating temperature (from 200 to 800°C) of Co catalysts before pyrolysis was studied. It was found that, as the preheating temperature of supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts was increased, the amount of synthesized carbon, including CFC, decreased because of  $\text{Co}^0$  deactivation due to the interaction with the support and coke formation.

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## INTRODUCTION

It is well known that iron subgroup metals (iron, nickel, and cobalt) are the most active catalysts for the synthesis of carbon nanofibers and nanotubes in the course of hydrocarbon pyrolysis [1, 2]. Among them, the best studied are Ni-containing catalysts prepared by either the coprecipitation of nickel and aluminum hydroxides [3–6] or the mechanochemical activation of corresponding metal oxide and hydroxide powders [7]. The nickel content of these catalysts is as high as 85–90 wt %, and the yield of carbon is  $\geq 100$  g/(g Ni) [8]. A few publications were devoted to the synthesis of carbon nanofibers/nanotubes on Co catalysts. Rakov et al. [3] found that two-, three-, and four-layer nanotubes having a conical cap were formed upon the pyrolysis of methane at 900°C on a Mo–Co–Mg (1 : 5 : 94) catalyst. Li et al. [9] prepared multiwall ( $\sim 10$  layers) carbon nanotubes open at one end by the pyrolysis of acetylene at 700°C on cobalt particles of size 100–200 nm, which were electrochemically deposited in the pores of  $\text{Al}_2\text{O}_3$  templates.

Previously, Kovalenko et al. [10] studied Co catalysts prepared by the homogeneous precipitation of Co hydroxide compounds onto aluminosilicate supports (ceramic foam and vermiculite) in the course of propane–butane pyrolysis in the presence of hydrogen. As a result of these studies, they prepared composite carbon–mineral adsorbents on the surface of which a thin

layer ( $\sim 1$   $\mu\text{m}$ ) of catalytic filamentous carbon (CFC) was synthesized. The yield of carbon was no higher than 40 (g CFC)/(g Co) [10, 13]. The applicability of the resulting adsorbents to the immobilization of Co-dependent enzymes was studied [10].

The aim of this work was to comparatively study the effect of the physicochemical properties of an aluminum oxide support on the formation and activity of Co-containing catalysts in the pyrolysis of propane–butane; to study the dependence of the yield of CFC on (1) the crystalline modification of aluminum oxide ( $\alpha$ - and  $\gamma$ - $\text{Al}_2\text{O}_3$ ) and (2) the preheating temperature (from 200 to 800°C) of supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts prepared by the homogeneous precipitation of Co hydroxide compounds in the presence of urea before the pyrolysis process; and to study the surface morphology of Co catalysts and surface carbon deposits using scanning electron microscopy.

## EXPERIMENTAL

The following commercial supports based on aluminum oxide (from OAO Katalizator, Novosibirsk) were used as the parent support for the preparation of supported Co-containing catalysts for propane–butane pyrolysis: KN-21 support ( $S_{\text{sp}} = 0.5$   $\text{m}^2/\text{g}$ ) as rings 5–6 mm in height with outer and inner diameters of 7 and 2 mm, respectively, and AOK-63-11 S support

Physicochemical characteristics of carbonized Co-containing catalysts depending on their thermal treatment before performing the process of propane–butane pyrolysis in the presence of H<sub>2</sub>

Catalyst*	T of pretreatment, °C	Co content, wt %	C <sub>Σ</sub> , wt %	Y, (g CFC)/(g Co)	S <sub>sp</sub> , m <sup>2</sup> /g	
					Co/Al <sub>2</sub> O <sub>3</sub>	C/Co/Al <sub>2</sub> O <sub>3</sub>
Co <sub>x</sub> O <sub>y</sub>	—	87.3	77.3	0.9	—	—
	300	—	38.1	0.5	—	—
	600	—	48.5	0.6	—	—
	800	—	49.8	0.6	—	—
Co/α-Al <sub>2</sub> O <sub>3</sub>	—	0.12	0.4	3.4	1.2	9.2
	200	0.08	0.3	3.8	—	2.0
	300	—	0.3	3.6	—	3.6
	600	—	0.2	2.8	—	2.8
	800	—	0.1	1.6	—	1.5
Co/γ-Al <sub>2</sub> O <sub>3</sub>	—	0.13	4.5	1.2	222	154
	200	—	2.7	—	—	—
	300	—	2.7	—	228	214
	600	—	1.7	—	206	198
	800	—	0.3	—	158	160

\* Granule size of 0.6–1.2 mm.

(S<sub>sp</sub> = 246 m<sup>2</sup>/g) as granules (balls) 0.63–1.25 mm in diameter.

For comparative studies, bulk catalysts were prepared based on the hydroxo compounds of cobalt, which were freshly precipitated from cobalt nitrate solutions with an ammonia solution at 20–22°C and washed with distilled water in the following manners: (1) by drying the hydroxo compounds of cobalt at 20–22°C in air for about a day and pelletization by pressing at an excess pressure of 150 atm (referred to as bulk Co<sub>x</sub>O<sub>y</sub>) and (2) by thorough mechanical mixing of parent support granules with ~1 and ~10% suspensions of freshly precipitated cobalt hydroxides followed by drying the granules at 20–22°C in air for about a day (referred to as Co<sub>x</sub>O<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub>). The Co/Al<sub>2</sub>O<sub>3</sub> supported catalysts were prepared by the homogeneous precipitation of the hydroxo compounds of cobalt from aqueous solutions of cobalt(II) nitrate (0.01 M) in the presence of a tenfold excess of urea (0.1 M) under conditions described elsewhere [10, 11]. The Co/Al<sub>2</sub>O<sub>3</sub> supported catalysts were heated in a muffle furnace at 200°C for 4 h and at 300, 600, and 800°C for 1 h before performing the pyrolysis of propane–butane. The concentration of cobalt (wt %) was determined by atomic absorption spectrometry (AAS) on an ASSIN instrument with a flame-ionization detector.

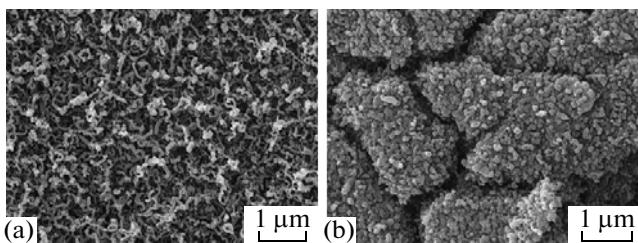
The pyrolysis of propane–butane in the presence/absence of hydrogen was performed in a system described elsewhere [10–12] at 600°C for 1 and 3 h. The gas mixture supplied to the reactor with the Co/Al<sub>2</sub>O<sub>3</sub> catalyst consisted either of propane–butane

(flow rate of 24 l/h) or of propane–butane and hydrogen (flow rate of 3 l/h).

The total amounts of carbon (C<sub>Σ</sub>, wt %) synthesized on the supports were determined by gravimetry as described previously [10–12]. It was found that, for the catalysts prepared based on the KN-21 support, the amounts of synthesized carbon determined from an increase (pyrolysis) or decrease (annealing) in the catalyst weight coincided within the limits of experimental error (0.1–0.2 abs. %); in this case, the parent support and prepared catalysts were nonhygroscopic. The hygroscopicity of catalysts prepared based on the AOK-63-11 support was determined after drying at 200°C for 4 h to constant weight. It was found that the parent AOK-63-11 support exhibited comparatively high hygroscopicity (≥5%). In this work, the values of C<sub>Σ</sub> determined by annealing are specified for all of the supports (table). In the calculation of this quantity, the weight loss of parent supports under conditions of annealing at 800°C for 4 h was taken into consideration.

The catalytic activity of cobalt was characterized by the yield of filamentous carbon (Y) as the ratio of the weight of synthesized CFC (in g) per gram of supported Co. The amount of synthesized CFC (in wt %) was estimated by difference C<sub>CFC</sub> = C<sub>Σ</sub> – C<sub>pyr</sub>, where C<sub>Σ</sub> is the total amount of carbon formed, wt %, and C<sub>pyr</sub> is the amount of pyrolytic carbon formed in the course of propane–butane pyrolysis on the parent support without supported cobalt, wt %.

The specific surface areas of the parent support (Al<sub>2</sub>O<sub>3</sub>), supported catalysts (Co/Al<sub>2</sub>O<sub>3</sub>), and carbon-



**Fig. 1.** Electron micrographs of the surfaces of  $\text{Co}_x\text{O}_y$  catalysts carbonized in the course of propane–butane pyrolysis for 1 h: (a) in the presence of hydrogen in the gas mixture ( $C_{\Sigma} = 77.3\% \text{ C}$ ) and (b) without hydrogen ( $C_{\Sigma} = 72.9\% \text{ C}$ ).

ized catalysts ( $\text{C}/\text{Co}/\text{Al}_2\text{O}_3$ ) were determined using the thermal desorption of argon on a SORBI-M instrument (ZAO Meta, Russia). The pore-size distribution was determined by mercury porosimetry on an AUTO-PORE 9200 instrument (Micromeritics, United States). The X-ray diffraction analysis of  $\text{Al}_2\text{O}_3$ ,  $\text{Co}/\text{Al}_2\text{O}_3$ , and  $\text{Co}_x\text{O}_y$  was performed on an HZG 4 diffractometer (Siemens, Germany).

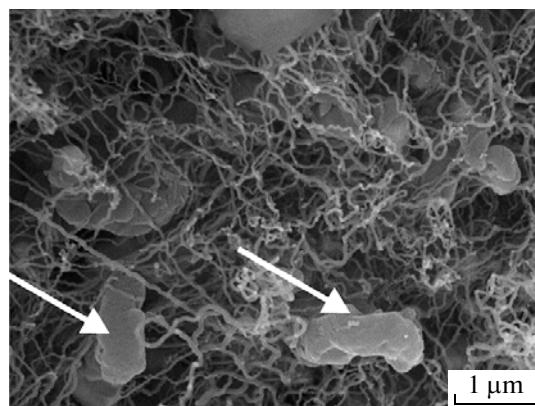
The electron-microscopic studies of the morphology of surface cobalt compounds and the synthesized carbon layer were performed with the use of JSM 6460 LV (JEOL, Japan) and LEO 1430 (LEO, Germany) instruments. Marks in the micrographs corresponded to distances in  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

X-ray diffraction data demonstrated that the parent KN-21 support ( $S_{\text{sp}} = 0.5 \text{ m}^2/\text{g}$ ) was  $\alpha$ -alumina, and a phase of  $\theta\text{-Al}_2\text{O}_3$  was detected in trace amounts (referred to as  $\alpha\text{-Al}_2\text{O}_3$ ). The AOK-63-11 S support ( $S_{\text{sp}} = 246 \text{ m}^2/\text{g}$ ) was a mixture of two phases,  $\gamma$ - and  $\chi\text{-Al}_2\text{O}_3$ , whose concentrations were 67 and 33%, respectively (referred to as  $\gamma\text{-Al}_2\text{O}_3$ ).

We determined the catalytic activity of the parent support (without supported Co) in the course of propane–butane pyrolysis in the presence of hydrogen. Under the test conditions ( $600^\circ\text{C}$ , 1–3 h), the  $\alpha\text{-Al}_2\text{O}_3$  support was almost not carbonized; the carbon content was no higher than 0.1%. The  $\gamma\text{-Al}_2\text{O}_3$  support was intensely carbonized; the amount of carbon ( $C_{\text{pyr}}$ ) was  $2.3 \pm 0.4\%$ . Based on the experimental data, we concluded that the catalytic activity of  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts was due to only the supported compounds of cobalt, whereas the observed activity of  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts was overall activity, which depended on the participation of both the initial support and supported cobalt in the process of pyrolysis.

To determine the role of an  $\text{Al}_2\text{O}_3$  support in the formation of a supported Co catalyst, we performed comparative studies of the catalytic activity of various Co-containing catalysts in the process of propane–butane pyrolysis.

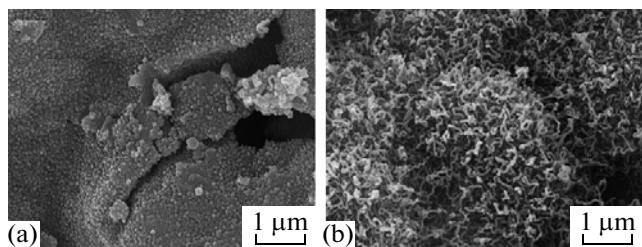


**Fig. 2.** Electron micrograph of the surface of a  $\text{Co}_x\text{O}_y$  catalyst carbonized in the course of propane–butane pyrolysis in the presence of hydrogen for 3 h ( $C_{\Sigma} = 86.2\% \text{ C}$ ).

We studied bulk  $\text{Co}_x\text{O}_y$  catalysts. Based on the results of chemical analysis, the Co content of  $\text{Co}_x\text{O}_y$  compounds prepared from freshly precipitated cobalt(II) hydroxides and heated under pyrolysis conditions ( $600^\circ\text{C}$ , 1 h) in a flow of nitrogen was 87.3%. The calculated Co contents of  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  oxides are 78.7 and 73.4%, respectively. X-ray diffraction analysis showed that the  $\text{Co}_x\text{O}_y$  catalysts were mixtures of the following three phases: cubic cobalt metal and  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  phases in commensurable amounts.

The catalysts were intensely carbonized in the course of propane–butane pyrolysis both in the presence of hydrogen and with no hydrogen. The amounts of carbon synthesized for 1 h were almost the same, 77.3 and 72.9%, respectively. Electron-microscopic studies demonstrated that carbon nanofibers were synthesized on  $\text{Co}_x\text{O}_y$  both in the presence of hydrogen and with no hydrogen (Fig. 1a). Upon the pyrolysis of propane–butane with no hydrogen, carbon deposits without an expressed fibrous structure were detected on the surface of bulk  $\text{Co}_x\text{O}_y$  along with carbon nanofibers (Fig. 1b). The yield of carbon was  $\sim 0.9 \text{ (g CFC)/(g Co)}$ .

As the time of propane–butane pyrolysis in the presence of hydrogen was increased (to 3 h), the total amount of carbon formed on  $\text{Co}_x\text{O}_y$  increased only slightly (by a factor of 1.1 to 86.2%). In this case, a comparison between Figs. 1a and 2 indicates that carbon nanofibers were considerably elongated. As the pyrolysis time was increased, rounded particles were also detected (Fig. 2, marked with arrows); it is likely that these were aggregated  $\text{Co}^0$  metal particles. It is well known that the reduction of cobalt oxides to  $\text{Co}^0$  in an atmosphere of hydrogen readily occurs at  $\sim 150\text{--}250^\circ\text{C}$ . It can be seen that, as the size of catalytically active  $\text{Co}^0$  particles was increased, the length of the synthesized carbon nanofiber increased. As the pyrolysis time was increased, the yield of carbon remained almost unchanged; it was estimated at  $\sim 1 \text{ (g CFC)/(g Co)}$ . Thus, cobalt as the constituent of  $\text{Co}_x\text{O}_y$  is a catalyst for the process of propane–butane pyrolysis



**Fig. 3.** Electron micrographs of the carbonized  $\text{Co}_x\text{O}_y/\alpha\text{-Al}_2\text{O}_3$  catalysts: (a) 0.05% Co,  $C_{\Sigma} = 2.9\%$ , 1-h pyrolysis and (b) 0.25% Co,  $C_{\Sigma} = 1.0\%$ , 3-h pyrolysis (granule cleavage).

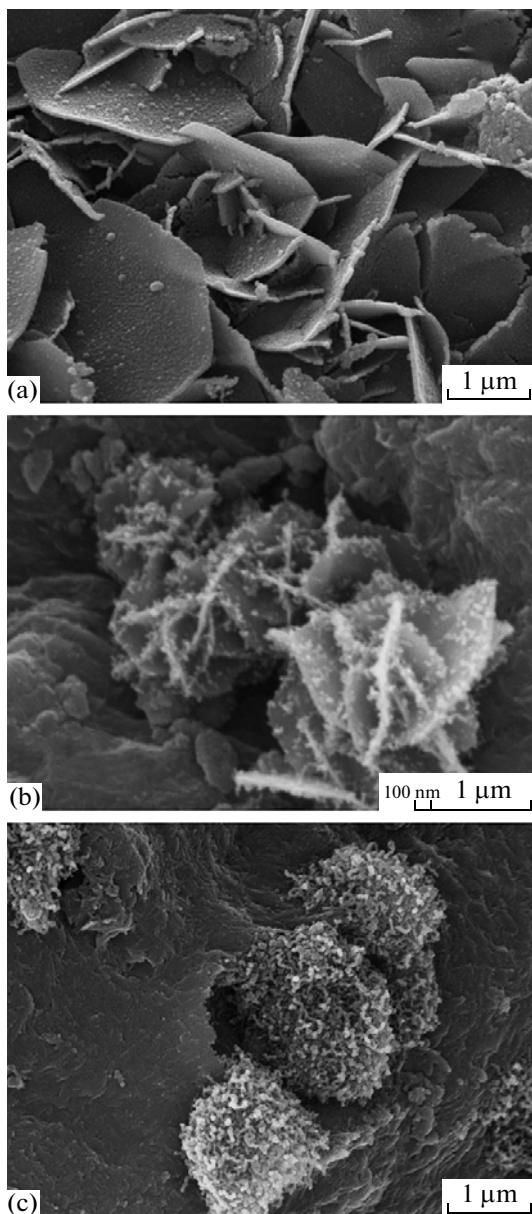
(even in the absence of hydrogen from the reaction gas mixture), which results in the synthesis of carbon nanofibers; in this case,  $Y \approx 1$  (g CFC)/(g Co).

We studied two-phase  $\text{Co}_x\text{O}_y/\alpha\text{-Al}_2\text{O}_3$  catalysts prepared by mechanically mixing freshly precipitated hydroxo compounds of cobalt(II) with  $\alpha$ -alumina granules (KN-21). Evidently, the amount of synthesized carbon increased with increasing the amount of the  $\text{Co}_x\text{O}_y$  phase, and a maximum carbon content was 9.0% at 11.1% Co. In this case, the yield of carbon was  $\sim 0.8$  (g CFC)/(g Co), which is close to  $Y$  for bulk  $\text{Co}_x\text{O}_y$ . As the cobalt content of the resulting catalysts was decreased, the yield of carbon increased, and it was 3.2 g/g at 0.25% Co. The most significant differences were detected in the morphology of a synthesized carbon layer. Upon pyrolysis for 1 h on the  $\text{Co}_x\text{O}_y/\alpha\text{-Al}_2\text{O}_3$  catalyst, carbon deposits without an expressed fibrous structure were formed, which were similar to the growth points of carbon nanofiber (Fig. 3a). As the time of pyrolysis was increased (to 3 h), deposits with a carbon nanofiber structure of various lengths (shorter and longer) were synthesized (Fig. 3b). Longer fibers were detected at cleavages within the granules of macroporous  $\alpha$ -alumina (Fig. 3b); this suggests a redistribution of cobalt compounds and the formation of active particles within support granules. As the pyrolysis time was increased, the electron micrographs of  $\text{Co}_x\text{O}_y/\alpha\text{-Al}_2\text{O}_3$  samples (unlike bulk  $\text{Co}_x\text{O}_y$ ) did not exhibit rounded  $\text{Co}^0$  particles. Thus, the effect of the support on the catalytic activity of  $\text{Co}_x\text{O}_y$  manifested itself in the prevention of the aggregation of  $\text{Co}^0$  metal particles and, as a result, in a decrease in the length of the synthesized carbon nanofiber. It is also interesting that carbon nanofibers were detected at the cleavages of catalysts prepared by mechanically mixing two solid phases ( $\text{Co(OH)}_2$  precipitate and  $\text{Al}_2\text{O}_3$ ).

We studied the supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts prepared by the homogeneous precipitation of the hydroxo compounds of cobalt in the presence of urea. According to AAS data, the concentrations of cobalt in these samples were 0.1–0.2%. The total amounts of carbon synthesized for 1 h by the pyrolysis of propane–butane in the presence of  $\text{H}_2$  on KN-21 rings

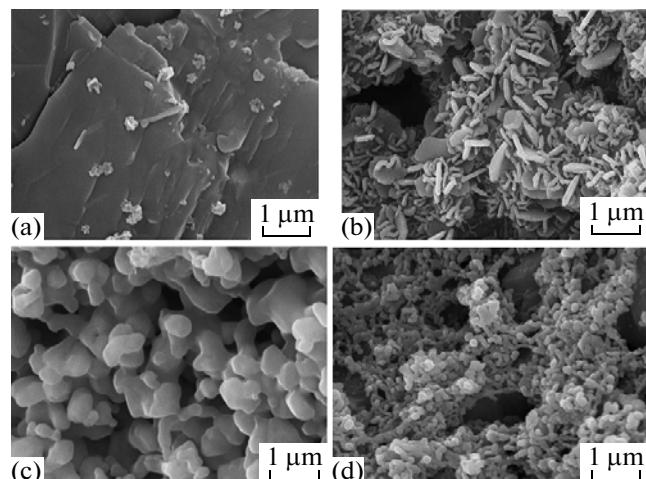
( $\alpha\text{-Al}_2\text{O}_3$ ) and AOK-63-11 balls ( $\gamma\text{-Al}_2\text{O}_3$ ) averaged over the entire granule were  $\sim 0.4$  and  $\sim 3\%$ , respectively. Note that the synthesis of carbon on alumina rings mainly occurred on the outer geometrical surface of a granule, and carbonized catalysts exhibited a shell structure. For the supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts prepared based on  $\alpha$ - and  $\gamma$ -alumina, the yields of filamentous carbon were 2.5 and  $\leq 1.2$  (g CFC)/(g Co), respectively ( $Y \approx 1$  g/g for bulk  $\text{Co}_x\text{O}_y$ ). Thus, the effect of the support on the properties of supported Co catalysts manifested itself, first, in the dependence of the yield of carbon on the crystal modification of an alumina support and, second, in an increase in  $Y$ , as compared with that of the bulk catalyst. It was found that the maximum yield of carbon was characteristic of catalysts prepared on an  $\alpha\text{-Al}_2\text{O}_3$  macroporous support. Previously [13], it was found that the main reason for the observed differences consists in the size of precipitated cobalt compound particles; thus, cobalt particles on macroporous  $\alpha\text{-Al}_2\text{O}_3$  were small, and their size was no greater than 1  $\mu\text{m}$ .

It was found that the total amount of carbon synthesized on the  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalyst was independent of pyrolysis time from 1 to 3 h. The electron-microscopic studies demonstrated that, regardless of pyrolysis time, deposits analogous to those shown in Fig. 3b with a pronounced carbon nanofiber structure were formed on the  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts. On the other hand, as the pyrolysis time was increased from 1 to 3 h, the total amounts of carbon ( $C_{\Sigma}$ ) on the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts increased by a factor of  $>2$  and were, on average,  $3.2 \pm 1.3$  and  $7.1 \pm 1.1\%$ , respectively. In Fig. 4a, it can be seen that, on these catalysts, rounded deposits as hillocks were formed at multiple points upon pyrolysis for 1 h on the surface of relatively coarse supported particles of cobalt compounds. These deposits were similar to the growth points of carbon nanofiber, at which carbon nanofibers can hypothetically grow under changes in pyrolysis conditions. However, as the time of pyrolysis on  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  was increased, either carbon deposits did not exhibit a pronounced fibrous structure (Fig. 4b) or carbon nanofiber bundles were locally formed (Fig. 4c). As noted above, the following two parallel processes occurred on the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts under conditions of propane–butane pyrolysis in the presence of hydrogen: (1) coke formation on the parent  $\gamma\text{-Al}_2\text{O}_3$  support and (2) CFC synthesis on Co. The electron-microscopic studies demonstrated that the surface of carbonized  $\text{C}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts was smoothed with pyrolytic carbon as the pyrolysis time was increased. Thus, as the time of pyrolysis on  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  was increased, pyrolytic carbon was mainly formed on the parent  $\gamma\text{-Al}_2\text{O}_3$  (process 1). Therefore, the effect of the support manifests itself in the fact that supported cobalt did almost not exhibit catalytic activity on mesoporous aluminum oxide (AOK-63-11), whereas cobalt supported onto macroporous aluminum oxide (KN-21) was active in the synthesis of carbon nanofibers.



**Fig. 4.** Electron micrographs of the carbonized  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts: (a) 0.13% Co,  $C_\Sigma = 4.5\%$ , 1-h pyrolysis; (b) 0.23% Co,  $C_\Sigma = 6.9\%$ , 3-h pyrolysis; and (c) 0.23% Co,  $C_\Sigma = 2.2\%$ , 3-h pyrolysis.

To determine the reasons for the observed differences, we performed comparative studies of the dependence of the activity of supported cobalt catalysts on both the crystalline modification of the parent alumina and the temperature of preheating before the process of pyrolysis. Initially, it was found that different colors appeared in annealed carbonized catalysts (after the determination of  $C_\Sigma$  by annealing at  $800^\circ\text{C}$  for 4 h). Thus, upon the annealing of  $\text{C}/\text{Co}/\alpha\text{-Al}_2\text{O}_3$ , a grey sample was obtained; it is evident that, in this case, cobalt occurred as the  $\text{Co}_3\text{O}_4$  compound. Upon the annealing of  $\text{C}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$ , the supports became



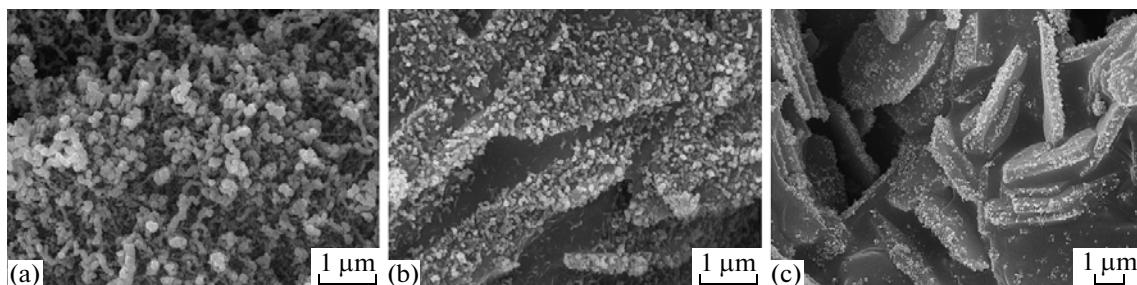
**Fig. 5.** Electron micrographs of the surfaces of (a, b) freshly prepared and (c, d) annealed catalysts: (a, c)  $\text{Co}_x\text{O}_y$  and (b, d)  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  (0.1% Co).

bright blue; this suggests the formation of cobalt aluminates  $\text{CoAlO}_4$ . However, X-ray diffraction analysis did not reveal reliable differences in the crystal structures of both parent supports and catalysts (freshly prepared and annealed); this was likely due to a low concentration of supported cobalt ( $\leq 0.2\%$ ).

Comparative electron-microscopic studies demonstrated that the surface morphologies of freshly prepared and annealed (at  $800^\circ\text{C}$ ) Co-containing catalysts were different. Thus, the surface of the bulk  $\text{Co}_x\text{O}_y$  catalyst completely changed its morphology from smooth (Fig. 5a) to that composed of rounded particles, which were likely formed from  $\text{Co}^0$  metal particles (Fig. 5c). In annealed  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts, the faces of supported Co hydroxo compound particles also became smoother and roundish (cf. Figs. 5b and 5d for  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ ).

We also found that the amount  $C_\Sigma$  of carbon newly synthesized on annealed supported catalysts decreased by a factor of 1.4–4.0. On annealed  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts, analogously to freshly prepared ones, carbon nanofibers were synthesized upon repeated pyrolysis. On annealed  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts, carbon deposits did not exhibit a fibrous structure. These results allowed us to conclude that the carbon-containing adsorbents prepared based on carbonized  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts, which were studied previously for the adsorption immobilization of enzymatically active substances [10, 13], cannot be regenerated by annealing and repeated pyrolysis.

To examine the deactivation of Co-containing (bulk and supported) catalysts, we performed comparative studies on the effect of the preheating of freshly prepared catalysts before pyrolysis on the amount of synthesized carbon, the yield of carbon, and the morphology of carbon deposits. For bulk  $\text{Co}_x\text{O}_y$  catalysts, we found that, first, unlike supported catalysts,



**Fig. 6.** Electron micrographs of the surfaces of carbonized  $\text{C}/\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts: (a) with no thermal treatment ( $C_{\Sigma} = 3.1\%$ ), (b) after catalyst preheating at  $600^{\circ}\text{C}$  ( $C_{\Sigma} = 0.22\%$ ), and (c) after catalyst preheating at  $800^{\circ}\text{C}$  ( $C_{\Sigma} = 0.13\%$ ).

annealed catalysts were intensely carbonized (the amount of newly synthesized carbon was 47.5%) and, second, an increase in the temperature of the thermal pretreatment of  $\text{Co}_x\text{O}_y$  before pyrolysis from 300 to  $800^{\circ}\text{C}$  had almost no effect on  $C_{\Sigma}$  and the yield of carbon (see the table). For all of the supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts regardless of the crystal structure of the support, it was found that the total amount of formed carbon decreased many times as the temperature of the thermal treatment was increased (see the table). The  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts twice heated at  $800^{\circ}\text{C}$  (heating  $\rightarrow$  pyrolysis  $\rightarrow$  annealing  $\rightarrow$  pyrolysis) did not exhibit catalytic activity: the amount of synthesized carbon was no higher than 0.1%. Thus, the observed differences were only due to the effect of the support on the catalytic activity of supported cobalt.

The following processes can be responsible for the deactivation of cobalt supported on alumina as the temperature was increased to  $800^{\circ}\text{C}$ : (1) particle growth due to redistribution and agglomeration, (2) deactivation due to the formation of catalytically inactive chemical compounds with the support, and (3) encapsulation of  $\text{Co}^0$  particles by pyrolytic carbon. The electron-microscopic studies demonstrated that the size of supported Co particles remained almost unchanged upon catalyst annealing at  $800^{\circ}\text{C}$  (Figs. 5b and 5d for  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ ). Therefore, process (1) does not make a considerable contribution to the deactivation of supported cobalt. As noted above, the annealed  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts became bright blue (for comparison, freshly prepared catalysts were almost colorless); that is, as the temperature was increased, the formation of cobalt aluminate, which did not exhibit catalytic activity in the synthesis of CFC, was observed (reason 2). Indeed, as noted above, bulk  $\text{Co}_x\text{O}_y$ , from which  $\text{Al}_2\text{O}_3$  was absent, did not change its catalytic activity as the preheating temperature was increased. The electron-microscopic images of the surfaces of  $\text{C}/\text{Co}_x\text{O}_y$  catalysts carbonized upon pyrolysis for 1 h regardless of preheating temperature fully coincided with the image in Fig. 2, where characteristic rounded particles of cobalt metal can be clearly seen.

As noted previously, the total amount of synthesized carbon  $C_{\Sigma}$  decreased as the preheating tempera-

ture of supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts before the process of pyrolysis (see the table). It is difficult to estimate the yield of CFC for  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  because  $C_{\Sigma} \approx C_{\text{pyr}}$ . For the  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts, the maximum yield of carbon was  $\sim 4$  (g CFC)/(g Co), and the value of  $Y$  decreased by a factor of  $\sim 2$  as the catalyst preheating temperature was increased from 200 to  $800^{\circ}\text{C}$  (see the table).

A comparative analysis of texture characteristics (see the table) demonstrated that the specific surface areas of all of the  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts was  $1.2 \text{ m}^2/\text{g}$ , whereas the  $S_{\text{sp}}$  of catalysts prepared based on  $\gamma\text{-Al}_2\text{O}_3$  decreased from 230 to  $160 \text{ m}^2/\text{g}$  as the preheating temperature was increased. In this case, as noted above, considerable differences in the crystal structures of the catalysts were not detected. In the synthesis of carbon on  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ , it was found that the specific surface areas of carbonized  $\text{C}/\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts increased by a factor of  $\sim 2\text{--}7$ , except for catalysts heated at  $800^{\circ}\text{C}$ . For carbonized  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts, the value of  $S_{\text{sp}}$  changed not very significantly; in this case, a maximum increase in  $S_{\text{sp}}$  was observed at a carbon content of  $\sim 2\text{--}3\%$ . At a carbon content higher than 3%, the specific surface area of  $\text{C}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$  decreased; this was likely due to the blocking of support mesopores by carbon coke deposits.

A comparison between electron-microscopic images exhibited differences in the morphology of synthesized carbon deposits depending on the preheating temperature of supported catalysts. Thus, as the preheating temperature was increased, the surface of carbonized  $\text{C}/\text{Co}/\text{Al}_2\text{O}_3$  catalysts smoothed because of the formation of vast regions of pyrolytic carbon. This allowed us to assume that reason 3 (coking and encapsulation of Co particles by carbon) can play an important role in the deactivation of the supported Co catalyst. As the preheating temperature of  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts was increased, not only a decrease in the length of carbon nanofiber (Figs. 6a–6c) but also the appearance of smooth surface regions (Fig. 6c) was observed. Thus, the interaction of Co with aluminum oxide with the formation of catalytically inactive compounds (which is especially characteristic of  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ ) and the encapsulation of active

$\text{Co}^0$  particles with pyrolytic carbon are the main reasons for the deactivation of supported Co catalysts.

## CONCLUSIONS

It was found that cobalt as a constituent of hydroxo compounds exhibited catalytic activity in the process of propane–butane pyrolysis in the presence of hydrogen at 600°C; in this case, carbon nanofibers were synthesized. The crystalline modification of aluminum oxide ( $\alpha$ - or  $\gamma$ -) exerted a considerable effect on the formation and catalytic activity of supported cobalt and on the morphology of carbon deposits. It was found that catalytic filamentous carbon was synthesized only on supported  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  catalysts prepared by the homogeneous precipitation of the hydroxo compounds of cobalt onto macroporous  $\alpha\text{-Al}_2\text{O}_3$  with a maximum yield of  $\sim 4$  (g CFC)/(g Co). Pyrolytic carbon deposits were mainly formed on  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts prepared by an analogous procedure on mesoporous aluminum oxide because of the high activity of the parent support in the process of propane–butane pyrolysis.

It was found that, upon the preheating of freshly prepared supported  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts before pyrolysis (from 200 to 800°C), the total amount of formed carbon decreased as the temperature of this preheating was increased. As found in electron-microscopic studies, the length of carbon nanofiber synthesized on  $\text{Co}/\alpha\text{-Al}_2\text{O}_3$  considerably decreased. The main reasons for the deactivation of supported Co catalysts are the formation of inactive cobalt aluminates and the encapsulation of cobalt particles by pyrolytic carbon.

Thus, both the chemical nature of the support ( $\text{Al}/\text{Si}$ ,  $\text{Al}_2\text{O}_3$ ) and the crystal structure of aluminum oxide exert considerable effects on the formation of an active Co catalyst for the synthesis of carbon nanofibers on the support surface in the course of the pyrolysis of hydrocarbons. Indeed, maximum yields of catalytic filamentous carbon on aluminosilicates (ceramic foam) and aluminum oxides ( $\alpha\text{-Al}_2\text{O}_3$ ) were

$\sim 40$  [10] and  $\sim 4$  (g CFC)/(g Co), respectively. The supporting of Co(II) compounds onto an inert macroporous support (corundum  $\alpha\text{-Al}_2\text{O}_3$ ) increased the activity of cobalt in the synthesis of CFC, on average, by a factor of 3, as compared with a bulk catalyst.

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