CATALYTIC PROPERTIES OF APPLIED POLYNUCLEAR COBALT COMPLEXES IN THE REACTION OF HYDROGENATION OF CO

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There are data which show that the size of metal particles affects not only the activity of the catalyst in Fischer—Tropsch synthesis but also the selectivity [1-5].

In this respect, the method of preparation of metallic catalysts by application of organometallic or carbonyl complexes on the surface of oxides [6-13], which permits obtaining a narrower size distribution of the metal particles on the surface due to the absence of the stage of reduction in comparison to the traditional method of application of the metal from a salt, has recently been widely used. In the last case, incomplete reduction takes place at an insufficiently high temperature, and caking of the particles is possible at high temperatures, resulting in a decrease in the metallic surface area.

When metal carbonyls are used for preparation of heterogeneous catalysts, the size of the metal particles on the surface of oxides can be regulated by altering the heating rate and activation temperature of the complex [4]. If the activation temperature of the complex is higher than its thermal stability temperature, then elimination of all CO ligands takes place and the metal atoms aggregate into clusters. According to the data in [4], the size of cobalt particles prepared by this method varied within the limits of 20-50 Å, i.e., clusters several tens of atoms in size were formed. Particles ∿20 Å in size were obtained in [5] by thermal decomposition of iron carbonyls, and they increased to 200-500 Å during the reaction.

The use of homogeneous complexes with a different number of metal atoms in the cluster for application is another possible way of altering the size of the metal particles on the surface of an oxide carrier. If there are organic ligands which are stable at the catalyst activation temperature in addition to CO ligands in such a complex, it is possible to hypothesize that they will prevent association of the metal atoms, and fragments of the starting complexes forming smaller clusters than in composition of carbonyls will exist on the surface. The applied organometallic carbonyl complexes are also convenient models for clarifying the role of different factors in catalysis: geometry and polynuclear character of the starting complexes, ratios of reduced and oxidized forms of the metal on the surface, degree of dehydroxylation of the surface of the oxide carrier.

A series of cobalt carbonyl complexes of different geometry and nucleation was selected and the effect of these factors and the degree of hydroxylation of the surface of Al_2O_3 on their activity and selectivity in Fischer—Tropsch synthesis was investigated in the present study. An attempt was made to elucidate the role of the organic ligand in formation of active particles on the surface. The method of temperature-programmed desorption* was used and the starting complex was synthesized on the surface of Al_2O_3.

EXPERIMENTAL

The catalytic properties of the applied cobalt complexes were studied in a microcatalytic flow setup equipped with a specially designed quartz reactor which permits preparing the catalyst *in situ*.

Brand A-64 γ-Al_2O_3 (S_{sp} = 180 m²/g, 0.5-1.0 mm fraction) was used as the carrier. The Al_2O_3 was treated with heat in a current of air and then He purified of oxygen directly in the reactor before the experiment. As the thermographic and gravimetric data showed, at 270°C only adsorbed H_2O is eliminated from the surface, and at 550°C, ∿60% of the hydroxyl groups are eliminated.

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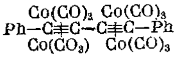
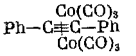
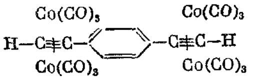
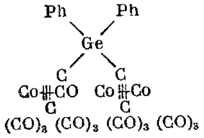
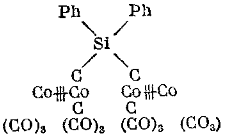
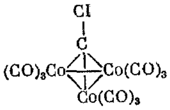
TABLE 1. Catalytic Properties of Applied Cobalt Carbonyl Complexes (T_{reac} = 220°C)

Complex		T_{tr}, Al_2O_3, °C	Conversion of CO, %	Yield,* %		
				CH_4	C_2-C_3 paraffins	C_2-C_3 olefins
	(I)	550 270	32 18	20,3 14,1	11,3 3,4	0,4 0,5
	(II)	550 270	23 20	14,4 9,0	8,3 9,5	0,3 1,5
	(III)	550 270	17 7	10,2 4,6	6,2 1,8	0,6 0,6
	(IV)	550	15	2,1	12,9	0
	(V)	550	17	3,0	14,0	0
	(VI)	550	5,6	3,5	2,1	0
$Co_2(CO)_8$	(VII)	550 270	49 39	25,6 16,7	23,3 22,0	0,1 0,3
Co(from $Co(NO_3)_2$, H_2, T = 400°, τ = 4 h)	(VIII)		8,0	1,9	4,5	0,2

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*The yield of products was calculated for the CO passed.

The organometallic carbonyl complexes were applied from solution in pentane at ∿20°C. The solvent was eliminated by flowing through an inert gas. After elimination of the solvent, the catalyst was heated to the reaction temperature (T_{reac}) in an inert gas current and a $CO-H_2$ mixture of 1:2 composition by volume was then delivered at a rate of 150 h^{-1}. The reaction was conducted for 5 h. The products of the reaction were analyzed chromatographically. CO_2 and C_2-C_3 olefins and paraffins were analyzed in isothermal conditions in a column with Porapack Q (1 m, t_{col} = 50°C); CO and CH_4 were analyzed in a column with BAU activated carbon (2 m, t_{col} = 90°C). The contribution of $>C_3$ hydrocarbons was $\leq$10%. All of the gases used in the experiments were first purified of traces of O_2.

Temperature-programmed decomposition (TPD) of the applied complexes was conducted in a setup which included a reactor with programmed heating, a chromatograph, and a mass spectrometer for analysis of the products of thermal desorption, a separator for separation of the products of desorption from He, and a multichannel loop oscillograph. Heating was conducted at the rate of 15 K/min, and the He flow rate was 60 cm^3/min.

RESULTS AND DISCUSSION

The data on the catalytic properties of the applied cobalt complexes, assessed by conversion of CO (x_{CO}) in steady-state conditions, are reported in Table 1. In all of the experiments, the concentration of cobalt was 2% and T_{reac} = 220°C. On the dehydroxylated surface, the smallest x_{CO} is observed on complex (VI). It is known [14] that the tetrahedral backbone of complex (VI) is very strong and is apparently not decomposed at T_{reac}, which results in catalysts with low activity. All of the other cobalt complexes studied contained the same structural fragment ($-C_2Co_2-$). If two such groups are positioned in a row [complex (I)], then x_{CO} is maximum. If the ($-C_2Co_2-$) groups are separated by a benzene ring (III), this results in a sharp decrease in x_{CO}, which is significantly lower than for one isolated group in (II). In complexes (IV) and (V) which contain fragments located far from each other in space, a lower x_{CO} is observed than in complex (I). The formation of a cluster with a number of metal atoms >2 is apparently necessary for obtaining a more active catalyst of Fischer-Tropsch synthesis.

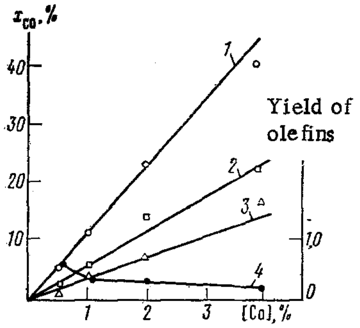

Fig. 1. Effect of [Co] on x_{CO} (1) and yield of CH_4 (2), C_2-C_3 paraffins (3), and olefins (4) in the reaction of hydrogenation of CO on complex (II).

The highest x_{CO} is observed for $Co_2(CO)_8$. In thermal activation of this complex, clusters with >4 metal atoms formed on the surface. The highest x_{CO} for complex (VII) in comparison to complexes (I)-(V) is apparently due to this; x_{CO} for complexes (I)-(V) is higher than for the catalyst prepared by reduction from a cobalt salt. The yield of CH_4, like the yield of other paraffins, varies as a function of the structure of the complex in the same sequence as x_{CO}.

As Table 1 shows, the initial structure of the complex also affects the selectivity of the process with respect to olefins, although the yield of olefins is low for all complexes. At T_{tr} = 550°C, the yield of olefins is highest for complex (III) (0.6%). Olefins are not formed on complexes (IV)-(VI). The yield of olefins in the experiments with $Co_2(CO)_8$ and catalyst (VIII) is low (0.1-0.2%).

The increase in the degree of hydroxylation of the surface of Al_2O_3 results in a decrease in x_{CO} for all of the complexes. The decrease in x_{CO} is not due to a decrease in the concentration of metal on the surface, which was determined by absorption spectroscopy. The yield of saturated hydrocarbons decreases. The yield of olefins for tetranuclear complexes changes insignificantly. At the same time, for the binuclear complex, an increase in the concentration of hydroxyl groups in the carrier increases the yield of olefins by more than three times. The effect of the concentration of complex (II) on x_{CO} and the selectivity is shown in Fig. 1. An increase in [Co] results in an increase in x_{CO}. The yield of CH_4 and saturated C_2-C_3 hydrocarbons increases, while the yield of olefins decreases.

The data thus show that the applied complexes have different catalytic properties. In this respect, the question arises concerning the form in which the complexes exists on the surface of the carrier after activation in an inert atmosphere and during synthesis of hydrocarbons. Two paths of activation of the complexes on the surface can be hypothesized: a) metal atoms are liberated from the ligands and form clusters in which the number of atoms is significantly higher than in the starting complex but is dependent on the size of the starting complex; b) the complexes form "subcarbonyl" particles on the surface whose structure reflects the structure of the starting complexes. The following experiments were conducted to clarify this question.

Experiments on TPD were conducted for complexes (I)-(III). Two intense peaks with T_{max} = 105 and 175°C were observed in the TPD spectra of all of the complexes. The analysis of the products of decomposition showed that the peaks on the TPD curves correspond to liberation of CO. No other products (except for a small amount of CO_2) were found up to 400°C. Both cobalt atoms and organic ligands are thus present on the surface in conditions of synthesis of hydrocarbons (200-220°C).

To answer the question of whether the organic ligands are bound with the cobalt atoms or carbonize the surface of the carrier, special experiments on synthesis of complex (II) on the surface of Al_2O_3 (T_{tr} = 550°C) from $Co_2(CO)_8$ and Ph_2C_2 (tolan) were conducted. Synthesis was conducted by two methods: Ph_2C_2 and then $Co_2(CO)_8$ were adsorbed on the surface of Al_2O_3 (method 1); adsorption of $Co_2(CO)_8$ and then Ph_2C_2 was then conducted (method 2). For comparison, the catalytic activity of applied complexes (II) and (VII) is also given in Table 2.

TABLE 2

	(VII)	Synthesis of (II) (method 1)	Synthesis (II) (method 2)	(II)
x_{CO}, %	49,0	35,6	25,0	23.3
Yield of olefins	0,1	0,2	0,4	0.3

Note that method of synthesis 1 yields a catalyst whose activity is close to (VII) while method 2 produced a catalyst with activity close to (II). With method of synthesis (1), $Co_2(CO)_8$ is apparently adsorbed on the surface of Al_2O_3 free of Ph_2C_2 and tolan plays the role of a modifier of the surface of the oxide. In method 2, Ph_2C_2 reacts with adsorbed $Co_2(CO)_8$, forming a complex.

The fact that the yield of olefins is lowest for complex (VII) indicates that either coating of the surface of the oxide with carbon or, more efficiently, hydroxyl groups (as the experiments with a different degree of surface hydroxylation showed) is necessary for increasing the yield of olefins. If hydrogen spillover (overflow of hydrogen between clusters through the oxide support) and transfer of active carbon play an important role during hydrogenation, then modification of the surface of the carrier with carbon or hydroxyl ligands will inhibit this process. This again emphasizes that the surface of the carrier actively participates in the process of catalysis. The data reported show that not only the polynuclear character of the complexes affects the structure of the centers formed during their decomposition but organic ligands also participate in their formation, preventing the formation of large clusters.

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CONCLUSIONS

1. The geometry and polynuclear character of initial homogeneous organometallic cobalt complexes affects the activity and selectivity of the applied catalysts of hydrogenation of CO prepared from them.

2. In the conditions of catalysis, the applied complexes almost totally lose the CO ligand, while the organic ligands participate in the formation of catalytically active particles.

3. The degree of hydroxylation of the surface of the oxide carrier affects the catalytic properties of the applied clusters.

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