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Effect of Thermal Treatment on the Structuring of an Iron–Cobalt–Chromium Oxide Catalyst for the Complete Oxidation of Fuel

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Abstract—Catalytic properties and structural aspects of the formation of iron–cobalt–chromium catalysts depending on the temperature of preliminary treatment are studied. A catalytically active iron–cobalt–chromium spinel is formed at a calcination temperature of 580–600°C. If catalytic packings are overheated in the course of hydrocarbon fuel oxidation or if temperatures above 700°C are used for preliminary treatment, the catalytic activity of the samples substantially decreases because an inactive solid solution of iron and chromium oxides with corundum structures is formed.

INTRODUCTION

It is known that different transition metal oxides, as well as spinels based on chromium, copper, nickel, cobalt, and iron, are active catalysts for the complete oxidation of hydrocarbons. They are actively used in the catalytic sources of heat [1, 2].

The synthesis of highly active and stable catalysts for the catalytic sources of heat depends on many factors, specifically on the preparation procedure, temperature, calcination time, support, etc.

Earlier we studied the catalytic properties and structural aspects of the formation of active and stable iron-cobalt-chromium oxide catalysts for the complete oxidation of hydrocarbons over wide ranges of their compositions [3], but we did not consider the effect of thermal treatment. However, heavy demands are made on the catalysts for the catalytic sources of heat. These demands are dictated by the conditions of catalyst service under which overheating of catalyst packing and alternating oxidative–reductive cycles of reaction medium action take place. Under the service conditions of the catalytic sources of heat, the time of stable catalyst operation decreases, and the catalyst packing is deactivated. After usual regeneration in a flow of air at a high temperature, the activity of the iron–cobalt–chromium catalyst drastically decreases.

In connection with this, it was interesting to study the conditions for preserving the active structures of these oxide catalysts during their preparation and use. In this work, we studied the effect of calcination, service time, and regeneration conditions on the process of structuring and catalytic properties of iron–cobalt–chromium catalysts for the complete oxidation of hydrocarbons. Moessbauer spectroscopy and X-ray phase analysis were used.

EXPERIMENTAL

Supported catalysts were prepared by the impregnation of silica plates with a solution of the corresponding nitrate with a certain concentration that maintained the preparation of samples with a desired composition. The samples were dried at 110–120°C and calcined in an air flow at 400–900°C. The amount of supported active phase (metal oxides) was 30% of the support weight. The composition of active components in the samples was as follows (in at. %): Fe, 65; Co, 10; Cr, 25. The degree of decomposition of initial nitrates was controlled by thermogravimetry using an MOM OD-3 instrument (Hungary) and taking a weighed 0.2-g sample.

The specific surface areas of the samples determined by low-temperature adsorption of argon was 6–12 m^2/g. After catalyst service, a decrease in the specific surface area was at most 7–10%.

Moessbauer measurements were carried out at 23 and –197°C using an electrodynamic-type setup [4] with a ^{57}Co source in a chromium matrix. Isomeric shifts were calculated with reference to the center of a hyperfine structure (hfs) of α-Fe. The parameters of Moessbauer spectra were processed using standard computer programs and the least-squares methods for the Moessbauer 3/2 ⟶ 1/2 transition. X-ray phase analyses were carried out at room temperature using a DRON 2 setup and FeK_α irradiation.

Catalytic properties were studied in the model CO oxidation reaction and in the complete oxidation of gasoline [3, 5].

CO oxidation was carried out using a pulse method in a microcatalytic reactor using a catalyst with a weight of 50 mg and a volume of 0.25 cm^3. The pulse volume was 0.7 cm^3 (0.2 cm^3 of CO and 0.5 cm^3 of air). The flow rate of helium was varied from 10 to 25 ml/min. The oxidation of gasoline was studied in a flow-type

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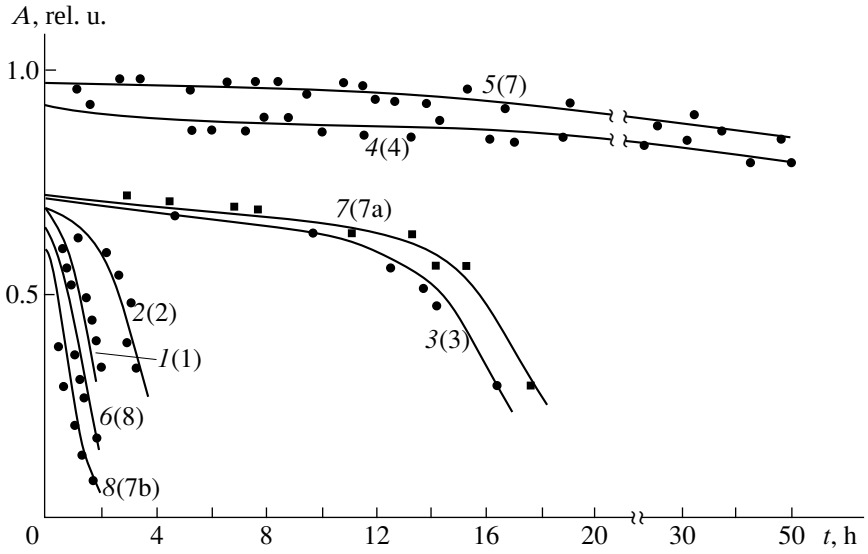

Fig. 1. Correlation between the activity (*A*) in the reaction of gasoline oxidation and catalyst service life calcined at (*1*) 400, (*2*) 450, (*3*) 500, (*4*) 550, (*5*) 600, (*6*) 900°C, (*7*) for the catalyst that worked in the catalytic source of heat for 1000 h, and (*8*) for the sample after regeneration. Numbers is parentheses correspond to the sample numbers in Table 1.

reactor with an air flow rate of 800 cm^3/min and a liquid gasoline rate of 0.047 g/min. The catalyst pellet had a diameter of 2 cm and a thickness of 1 cm. The catalyst weight was 0.6–0.7 g. The catalyst activity (*A*) was estimated from the conversion of gasoline on a given sample normalized to 90% conversion.

RESULTS AND DISCUSSION

Table 1 shows data on the effect of calcination temperature on the catalytic properties of samples in CO oxidation and the structuring of iron–cobalt–chromium catalysts. Figure 1 correlates the activity and the time of catalyst service in the complete oxidation of gasoline for different calcination temperatures (all curves are normalized to a constant value obtained at 90% conversion). As is seen from Fig. 1, the most stable samples were obtained by thermal treatment at 550–600°C (curves *4* and *5*). If calcination was carried out outside of this temperature range, the catalysts were unstable and less active. To determine the effect of catalytic reaction and further catalyst regeneration on the sample structure, sample 7 (curve *5*), which is the most active and stable, was treated by the reaction medium (gasoline and air) for 1000 h under real operation conditions of the catalytic sources of heat (sample 7a, Table 1, and

Table 1. X-ray phase data for iron–cobalt–chromium oxide catalysts calcined at different temperatures, and their catalytic properties in CO oxidation

Sample no.	Calcination temperature, °C	Temperature of 3–5% conversion of CO*, °C	Structure and parameters of spinel unit cell, Å
1	400	Inactive**	X-ray amorphous
2	450	Inactive	X-ray amorphous
3	500	Inactive	Spinel (8.36)
4	550	400–420	Spinel (8.35)
5	565	270–280	Spinel (8.35)
6	585	250–260	Spinel; corundum traces
7	600	250–260	Spinel (8.29) + corundum
8	900	280–290	Spinel (8.35) + corundum
7a	After 1000-h operation	Activity is substantially lowered	Spinel (8.37) + CoO
7b	After regeneration in a flow of air at 600°C	Inactive	Spinel (8.38) + Cr_2O_3

* At higher conversions, the reaction transfers to the region of an abrupt increase in the temperature and conversion because of the drastic evolution of heat. This temperature characterizes "catalyst ignition," after which oxidation transfers to the combustion regime [5, 7, 8].

** Catalyst was considered inactive if the ignition temperature was higher than 500°C.

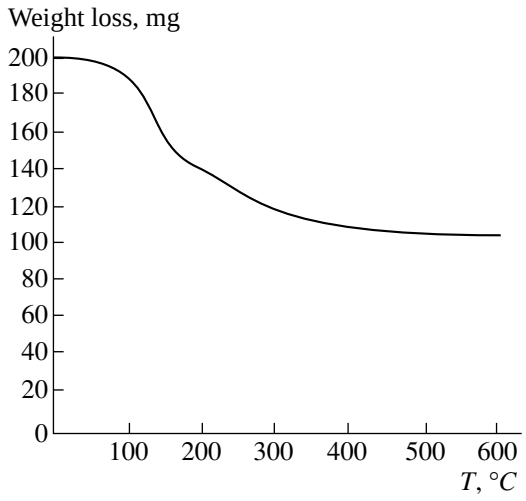

Fig. 2. Thermogravimetric curve of the initial Fe–Co–Cr–O sample.

curve *7* in Fig. 1). Sample 7b in Table 1 corresponds to sample 7a after its regeneration in a flow of air at 600°C (curve *8*).

As follows from Fig. 1 (curves *5* and *7*), the catalyst activity drastically decreases after the reaction of complete gasoline oxidation for 1000 h. An attempt to additionally recover the catalyst in a flow of air at 600°C resulted in the complete deactivation of the sample (Fig. 1, curve *8*). Comparison of the data in Fig. 1 and Table 1 shows that, with a change in the calcination temperature, the sample activities in CO oxidation and the complete oxidation of gasoline change in a similar way.

According to thermogravimetric data (Fig. 2), after sample calcination at 300°C, the main process of salt decomposition is virtually completed, although some insignificant weight loss continues up to 500°C, which is associated with the continuous removal of residual water and nitrogen oxides. These facts point to the incompleteness of the process of catalyst structuring and agree with X-ray phase analysis data showing that samples calcined a temperatures below 500°C are X-ray amorphous.

The calcination of samples at 500°C or at a higher temperature results in the formation of the phase of nonstoichiometric iron–cobalt–chromium spinel with a unit cell parameter of 8.29–8.36 Å. At a calcination temperature of 600°C, traces of a corundum phase are formed in addition to spinel. In the sample calcined at 900°C, we also observed two phases, but the corundum phase dominated (see Table 1).

Figure 3 shows typical Moessbauer spectra of the samples obtained at different calcination temperatures. The parameters of the spectra were measured at 25 and –197°C and summarized in Table 2: effective magnetic field strength (H_{eff}), line width (Γ), isomeric shift (δE), and the value of quadrupole splitting (ΔE_Q).

As can be seen from Fig. 3, the form of spectra change with an increase in the calcination temperature: it changes from the "paramagnetic" doublet, which is characteristic of the spinel structure, to the spectrum consisting of six lines and corresponding to the corundum-type oxide phase. The Moessbauer spectra of sample 1 measured at 23 and –197°C (spectrum *1* in Fig. 3) are doublets with broadened lines from the high-spin Fe^{3+} ion surrounded by the octahedron of oxygen atoms. An increase in the calcination temperature to 450°C did not change the form of the spectrum if measured at room temperature. However, at –197°C, it is characterized by magnetic hfs with rather broad non-Lorentz forms (Fig. 3, spectrum *2*).

In the low-temperature spectrum (see Table 2) of sample 5 obtained by calcination at 565°C, lines from another hfs appear, which have parameters characteris-

Table 2. Characteristic parameters of Moessbauer spectra of iron–cobalt–chromium catalysts obtained at different calcination temperatures

Sample no.	Calcination temperature, °C	Spinel structure								Corundum structure								
		23°C*			–197°C*				Phase amount, %	23°C*				–197°C*				Phase amount, %
		δE, mm/s	ΔE_Q, mm/s	Γ, mm/s	δE, mm/s	ΔE_Q, mm/s	Γ, mm/s	H_{eff}, kOe		δE, mm/s	ΔE_Q, mm/s	Γ, mm/s	H_{eff}, kOe	δE, mm/s	ΔE_Q, mm/s	Γ, mm/s	H_{eff}, kOe	
1	400	0.33	0.82	0.56	0.38	0.99	1.19		100	–	–	–	–	–	–	–	–	–
2	450	0.33	0.80	0.56	0.42	–0.02	1.78	454	100	–	–	–	–	–	–	–	–	–
3	500	0.33	0.85	0.71	0.44	–0.02	1.51	469	100	–	–	–	–	–	–	–	–	–
4	550	0.33	0.87	0.79	0.42	0.00	1.50	466	100	–	–	–	–	–	–	–	–	–
5	565	0.31	0.89	0.87	0.42	0.02	1.46	474	97	–	–	–	–	0.49	0.20	0.30	520	2–3
6	585	0.31	1.00	1.02	0.42	0.00	1.26	482	90	0.37	0.16	0.58	495	0.46	0.21	0.28	526	10
7	600	–	–	–	0.42	0.01	1.15	486	59	0.38	0.20	0.58	498	0.47	0.20	0.35	526	41
8	900	–	–	–	0.36	–0.02	0.96	494	27	0.38	0.19	0.45	499	0.47	0.20	0.34	528	73

* Temperature for spectrum recording.

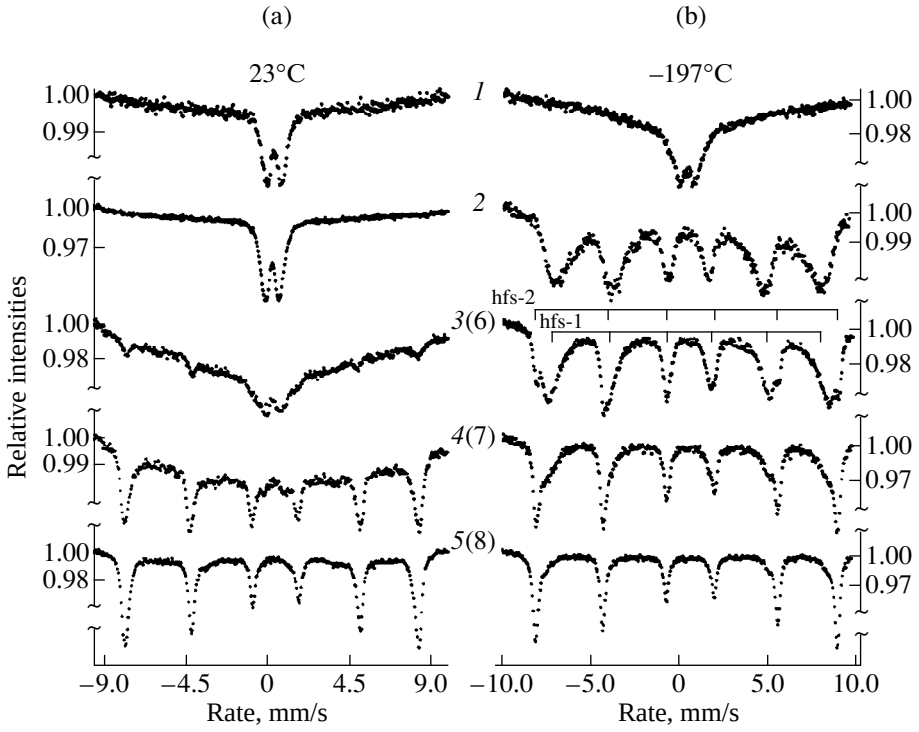

Fig. 3. Moessbauer spectra recorded at (a) 23 and (b) –197°C of iron–cobalt–chromium catalysts calcined at (*1*) 400, (*2*) 450, (*3*) 585, (*4*) 600, and (*5*) 900°C. Numbers is parentheses correspond to the sample numbers in Table 1.

tic of the Fe^{3+} ion in a lattice of defective or doped hematite [3]. Starting from a calcination temperature of 585°C, a sacciform region of the broad component of the resonance absorption of these structures appears in the spectra recorded at 25°C (Fig. 2, spectrum *3*). At a measurement temperature of –197°C, the average value of H_{eff} gradually increases (Table 2).

The spectra of samples calcined at 585°C contain clearly seen hfs lines from iron ions belonging to the hematite-phase mixed oxide $(Fe_{1-x}Cr_x)_2O_3$ [3]. According to X-ray diffraction data, the broadened Bragg reflection from the hematite phase with a corundum structure is identifiable only if the calcination temperature was higher than 585°C.

Available literature data [6] and our findings in this work and in [3] suggest that at calcination temperatures of 400–550°C, a one-phase composition of chemically inhomogeneous ternary spinel (triple ferrite) is formed in the iron–cobalt–chromium phase. Other structures were not detected by Moessbauer spectroscopy and X-ray phase analysis. With an increase in the temperature of thermal treatment from 400 to 550°C, only the crystallinity of the matrix increases. This leads to an increase in the ferrite Curie temperature, a decrease in the line width of magnetic hfs, and the appearance of first broad and then narrower Bragg diffraction lines. The non-Lorentz form of magnetic hfs lines points to the inhomogeneity in the local surround of the Moessbauer nucleus corresponding to some scattering of the H_{eff} values.

The thermal treatment of Fe–Co–Cr–O samples at temperatures higher than 550°C results in the appearance of the corundum phase of α-solid solution. With an increase in the calcination temperature to 900°C, the relative concentration of the corundum component increases because of the ternary ferrite decomposition. Thus, starting from some critical calcination temperature for this system, the catalysts contain two radically different phases: cubic mixed-oxide spinel and corundum oxide.

The above data suggest that the composition of ternary spinel changes with an increase in the temperature of thermal treatment. Below 550°C, all three oxides form a ternary system. With an increase in the calcination temperature of initial samples, some portions of iron and chromium ions leave the structure of triple ferrite and form the α-solid solution with a corundum structure. As this takes place, the concentration of cobalt in the spinel phase increases. At calcination temperatures ranging from 580 to 600°C, the component ratios became optimal from the standpoint of the maximal catalytic activity.

In the thermal treatment of samples or sample surface overheating during the reaction (over 600°C), the iron–cobalt–chromium ferrite decomposes, and the catalyst is completely deactivated. Changes in the Moessbauer parameters point to the prevailing formation of α-solid solutions based on iron and chromium oxides and iron–cobalt ferrite at elevated temperatures (700–900°C).

The individual oxides of iron, cobalt, and chromium can also be formed.

Sample 8 (Table 2) was additionally studied by the method of conversion Moessbauer spectroscopy. Using this variant of Moessbauer spectroscopy, we studied the surface of oxide film supported on a cathode of the proportional counter to estimate the apparent geometric surface area to the depth of 2000 Å independently of the size of specific catalyst particles. In this case, we only found a corundum-type solid solution. Thus, the α-solid solution based on iron oxide doped with chromium is formed as a cover of the spinel structure with a width of at least 2000 Å. Therefore, we conclude that catalyst deactivation is not only due to the decomposition of ternary ferrite, but also to the spinel surface blocking by the inactive oxide. The regeneration at elevated temperatures only favors further occurrence of these processes, which deactivate the catalyst. Data from X-ray phase analysis for samples 7a and 7b (Table 1) support the formation of individual oxides during operation and further regeneration of iron–cobalt–chromium oxide catalysts.

Thus, the results obtained in the study of iron–cobalt–chromium oxide catalysts by Moessbauer spectroscopy and X-ray phase analysis reveal one of the main reasons for a decrease in their activity and service life when the catalyst packings are overheated or when the catalysts are deactivated during its regeneration in air at 600–650°C. This is observed when the catalysts operate in the catalytic sources of heat. We also suppose that the introduction of additives that prevent the isolation of chromium and iron ions from the structure of the ternary ferrite and stabilize the catalytically active spinel-type structure would also result in an increase in the thermal stability and service life of the catalysts.

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