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CATALYSIS =

Synthesis of Cement-Containing Nickel–Copper Catalytic Systems Using Formic Acid Aqueous Solutions

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Abstract—Regular trends in the formation of phase composition, structure, and mechanical strength of nickel–copper catalysts used for treatment of process and off-gases were considered in relation to the concentration (5.0-60.0 wt %) of formic acid aqueous solutions used in their preparation. The optimal conditions of the preparation process were determined.

In modern industrial installations, oxygen is removed from process gases with platinum and palladium catalysts, the use of which is limited by high cost and short supply of these metals. A series of NKOtype cement-containing nickel–copper catalysts were developed¹ [1] for a wide range of catalytic processes, in which PK and APK catalysts with platinum and palladium active components are the most active. As opposed to these catalysts, the use of NKO-type catalysts requires their preliminary reduction by a hydrogen-containing gas at $350-450^{\circ}$ C. In some cases it is difficult to provide such temperatures in the existing installations.

The goal of this work was to develop a mechanically strong and highly active nickel–copper catalyst, which can be activated in an inert medium at low temperatures (180–280°C).

There are various procedures for the preparation of nickel–copper catalytic systems. These procedures mainly consist in deposition of an active component on a support by impregnation, coprecipitation, or fusion of catalyst components and mixing active components with the support.

Published data on the use of salts of carboxylic acids and of carboxylic acids themselves as liquid reagents in catalyst production suggest the possibility of obtaining supports and also high-performance catalysts that are activated at low temperatures ($150-250^{\circ}C$) in a stream of inert gases.

There are three main directions of using carboxylic acids in catalyst production: for preparing high-performance catalyst supports [2-6], for synthesizing catalytic systems [7–14], and for regenerating dead catalysts [15–18].

EXPERIMENTAL

As the raw material we used substances applied in the synthesis of cement-containing nickel-copper catalytic systems: nickel(II) (NSC) and copper(II) (CSC) subcarbonates, and technical-grade calcium aluminate (talum), which is a mixture of calcium monoaluminate (CaO·Al₂O₃, CA) and dialuminate (CaO·2Al₂O₃, CA₂). Samples were synthesized by mixing the initial components in the presence of formic acid aqueous solution, the concentration of which was varied within 5.0-60.0 wt %. The mixing (liquid : solid ratio from 1 : 1 to 1.5 : 1) was carried out at $60-80^{\circ}$ C. The catalyst mass with 15-20%moisture content was dried at 100° C, crushed, and pressed at 650 MPa into cylindrical pellets 6.0 mm in diameter and 5.0 mm high.

The X-ray phase analysis (XPA) of the samples was carried out on a DRON-2 diffractometer with CuK_{α} radiation, and the thermogravimetric analysis, on a Q-1500 D derivatograph. The stages of phase formation in inert media were studied in the linear heating mode on a thermochromatographic installation. The specific surface area was measured on a Tsvet-211 device by thermal desorption of argon. The mechanical strength was determined by crushing granules with application of load on their faces. The catalytic activity in oxygen hydrogenation was studied under atmospheric pressure on a laboratory flowthrough installation with a four-channel reactor. The input gas mixture contained 2.0 vol % O₂, 6.0 vol % H₂, and remainder argon. The tests of the catalytic activity were carried out at the space velocity of

¹ Developed at the Novomoskovsk Institute of Nitrogen Industry.



Fig. 1. DTG curves of samples treated with 40% aqueous solution of formic acid: (1) CSC, (2) NSC, (3) 50 wt % CSC + 50 wt % NSC, (4) CaCO₃, (5) γ -Al₂O₃, and (6) talum. (*T*) Temperature; the same for Fig. 2.

 6000 h^{-1} . The degree of oxygen conversion was taken as a measure of the catalytic activity.

The characteristic decomposition temperature of the initial NSC NiCO₃·2Ni(OH)₂·4H₂O is 320°C. The specific surface area of NiO obtained by NSC calcination does not exceed 40 m² g⁻¹. The compound CuCO₃·Cu(OH)₂ (CSC) decomposes at $T_{\text{max}} = 280^{\circ}$ C to CuO, which has disordered crystal lattice and specific surface area of no more than 10– 20 m² g⁻¹.

According to the XPA data, treatment of the initial NSC with formic acid gives nickel formate $Ni(HCOO)_2 \cdot 2H_2O$, and treatment of CSC, anhydrous copper formate $Cu(HCOO)_2$.

Figure 1 shows the rates of the weight loss by samples of NSC, CSC, and their mixture (50 wt % NSC-50 wt % CSC) treated with 40% aqueous solution of formic acid under conditions similar to the conditions of the synthesis. Nickel formate decomposes in two stages (Fig. 1, curve 2). The first stage (230°C) corresponds to the loss of water of crystallization, and the second (290°C), to exhaustive decomposition of nickel formate, which passes at a high rate, as shown by the intensity of the second peak. The further heating of the sample in the oxidizing atmosphere results in oxidation of the formed nickel (370°C). Copper formate (Fig. 1, curve I) decomposes in one stage (180°C). The resulting metallic copper is oxidized first to Cu₂O (220°C) and then to CuO (355°C).

It is known [19] that salts of carboxylic acids and, in particular, nickel and copper formates decompose in oxidant-free media to give metals. The decomposition of these salts is exothermic and occurs with a high rate at relatively low temperatures.

The decomposition temperature of formates can be considerably lowered [20] by adding a formate with a lower decomposition temperature. The decomposition of a mixture of Ni(II) and Cu(II) formates (Fig. 1, curve 3) is characterized by two intensive exothermic peaks. The exothermic effect at $T_{max} = 180^{\circ}$ C is due to decomposition of Cu(HCOO)₂ and dehydration of Ni(HCOO)₂ · 2H₂O, and that at $T_{max} = 215^{\circ}$ C, to decomposition of Ni(HCOO)₂. Thus, the presence of copper formate in a sample decreases the decomposition temperature of nickel formate from 290 to 215°C. At the same time, it cannot be ruled out that a double Cu(II) and Ni(II) salt such as CuNi(HCOO)₂·2H₂O can form under the experimental conditions of processing the NSC and CSC mixture [21]. This salt can also decompose in two stages.

To understand phase formation processes occurring in the course of the synthesis of cement-containing nickel-copper catalytic systems, we studied samples obtained by treatment of active aluminum oxide, CaCO₃, and calcium aluminate with a 40% aqueous solution of formic acid. The DTG curves of these samples are shown in Fig. 1. The experimental data indicate that treatment of aluminum oxide and $CaCO_3$ with HCOOH yields anhydrous aluminum and calcium formates (Fig. 1, curves 4, 5). In the case of treated talum (curve 6), the peak at 300°C corresponding to the decomposition of aluminum formate prevails. Furthermore, two exothermic peaks were recorded at 350 and 420°C, which are characteristic of the calcium formate decomposition. The endothermic peak at 790° C corresponds to the decomposition of CaCO₃ formed by calcium formate thermolysis. The effect of heat treatment on the specific surface area of talum $S_{\rm sp}$ (m² g⁻¹) treated by aqueous solution of formic acid is given below.

This dependence passes through a maximum $(140 \text{ m}^2 \text{ g}^{-1})$ at 280°C. When preparing cementcontaining nickel–copper catalytic systems (25 wt % NiO–10 wt % CuO–65 wt % talum), we found that, at

<i>T</i> , °C	$S_{\rm sp}, \ {\rm m}^2 \ {\rm g}^{-1}$
150	5.0
200	10.0
220	25.0
250	70.0
280	140.0
300	135.0
350	80.0
400	45.0

room temperature, the reaction of a mixture of the initial components (NSC + CSC + talum) with an aqueous solution of formic acid occurs at a relatively low rate, which reaches a maximum at 70-75°C. This temperature is optimal for the reaction of the mixture of components and also of each component separately with an aqueous solution of formic acid. For comparison, we prepared a catalyst sample (no. 1) using distilled water. The experimental data obtained by derivatography (Fig. 2) and by X-ray phase analysis allowed us to subdivide the samples under study in three groups depending on the concentration (%) of formic acid aqueous solution used in the stage of mixing: no. 1, H₂O, no. 2, 5.0, and no. 3, 10.0 (first group); no. 4, 15.0, no. 5, 20.0, no. 6, 25.0, and no. 7, 30.0 (second group); and no. 8, 40.0, no. 9, 50.0, and no. 10, 60.0 (third group).

The study of thermal transformations of the samples (Fig. 3) allowed us to establish the sign of thermal effects, determine a mode of heat treatment, and, using also the XPA data, identify phases formed in the course of the preparation. Thermal transformations of all the samples under study involve weight loss, its value increasing as the concentration of HCOOH is increased. The XPA data show that sample no. 2 is almost identical to sample no. 1. The phase composition of these samples includes NSC and CSC, mixed nickel and copper subaluminate, CuO, CaO · Al₂O₃, CaO 2Al₂O₃, and a minor amount of nickel, copper, aluminum, and calcium formates (for sample no. 2). The increase in the HCOOH concentration to 10% (sample no. 3) results in increased conversion of the initial components. Sample no. 5 prepared by treatment with 20% HCOOH solution considerably differs in the phase composition from the previous samples. In its phase composition, two types of nickel and copper subaluminates dominate: (1) standard Ni(II) and Cu(II) subaluminates (SA-I) having basic interplanar spacings d = 7.6 and d = 3.8 Å, respectively; (2) Ni(II) and Cu(II) subaluminates differing from standard subaluminates by the fact that their structure contains an additional anion (HCOO)⁻ (SA-II). They are characterized by the basic interplanar spacings d = 11 and d = 5.5 Å, respectively.



Fig. 2. DTG curves of catalyst samples prepared using aqueous solutions of formic acid. HCOOH concentration (%): (1) 0, (2) 5, (3) 20, and (4) 30.

Metal subaluminates can contain various anions replacing their OH⁻ groups [22], e.g., CO₃²⁻, NO₃⁻, etc. The formula of SA-I in the general form can be written as $MAl_2(OH)_8$ (M = Ni, Cu, Zn, Mg, etc.), and the formula of SA-II, as $MAl_2(OH)_{8-x}(HCOO)_x$, i.e., as a metal subaluminate formate.

A number of well pronounced effects due to the decomposition of SA-II-type compounds and also of Ni(II) and Cu(II) formates were detected in the range 120-280°C for sample no. 5 (Fig. 2, curve 3).

The further increase in the acid concentration to 30% (Fig. 2, curve 4) results in preferential formation of compounds such as SA-II, i.e., of Ni(II) and Cu(II) subaluminoformates. Furthermore, in this sample the amount of the formed Ni(II), Cu(II), Al(III), and Ca(II) formates increased, and a certain amount of NSC, CA, CA₂, CuO, and CaCO₃ was present.

The phase composition of sample no. 8 contains mainly Ni(II), Cu(II), Al(III), and Ca(II) formates; only small amounts of Ni(II) and Cu(II) subaluminate formates were detected. The use of a 50% aqueous solution of the acid (sample no. 9) promotes the formation of Ni(II), Cu(II), Al(III), and Ca(II) formates. The further increase in the acid concentration to 60% does not affect the phase composition. The phase of $CaCO_3$, which is a product of the exchange reaction of NSC and CSC with talum in the mixing stage, was detected in all the samples. The heat treatment of the samples increases the content of this phase. An additional amount of CaCO₃ is formed as a result of the decomposition of Ca(II) formate.

One of the main stages in formation of an active catalytic structure is the catalyst activation, and such characteristics as catalytic activity, mechanical strength, and service life depend on the conditions of this stage.

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Fig. 3. Thermochromatograms of catalyst samples prepared using aqueous solutions of formic acid and activated in (a) helium and (b) hydrogen. (I_{rel}) Relative intensity and (*T*) temperature. Concentration of HCOOH (%): (*1*) 5, (2) 30, (3) 40.

We studied reduction of the samples on a thermochemical installation allowing temperature-programmed reduction in various gas media and temperature modes. The curves of temperature-programmed reduction at linear heating rate of 5 deg min⁻¹, obtained in helium and hydrogen streams, respectively, are shown in Figs. 3a and 3b. These data show that the thermolysis of samples in a helium stream is in fact the stage of their activation. This process, which occurs in the range 125–400°C, is multistage. We can subdivide the samples under study into three groups with respect to the nature of activation. Sample nos. 2 and 3 comprise the first group, for which the main activation process takes place in the range 200–400°C with a rather small intensity. The second group (sample nos. 4 and 5) is characterized by occurrence of the activation in three stages (130–170, 200-300, and 300-400°C). In the third group, the activation is more intense and involves two stages (170-190°C and 215-225°C), corresponding to the decomposition of nickel and copper formates in an

inert gas stream. The temperature-programmed reduction data well correlate with the data of the X-ray phase and thermal analyses.

After activation, samples were cooled in a helium stream to room temperature and then heated in a hydrogen stream in a linear heating mode (Fig. 3b). For comparison, we studied simultaneously sample no. 1 prepared with distilled water. At temperatures below 300°C, no effects corresponding to the reduction of active components were detected, which suggests that the catalysts were completely activated in the inert gas stream. For all the sample under study, the curves of temperature-programmed reduction in hydrogen contain a single strong peak in the range 350-550°C, which corresponds to the low-temperature catalytic decomposition of calcium carbonate [23]. The shift of $T_{\rm max}$ of decomposition of this phase, as compared to this effect in sample no. 1, results from the presence of dispersed nickel and copper with a highly developed surface in all the samples except for sample no. 1.

The specific surface area, mechanical strength, and catalytic activity of samples reduced with hydrogen are given in the table. We chose the activation temperatures taking into account the data of the thermogravimetric, X-ray, and thermochromatographic analyses.

Products of the talum hydration and of its reaction with nickel and copper subcarbonates, and partially products of the decomposition of nickel and copper formates make the major contribution to the surface area development in sample no. 2, whereas in sample nos. 4-10 these are products of the decomposition of nickel and copper subaluminoformates (SA-II) and subaluminates formates (SA-I). In these samples the specific surface area, which was measured by argon thermal desorption on a Tsvet-211 instrument, is the total active surface area of nickel and copper. The fact that this surface area mainly corresponds to the active components is confirmed by the data on the surface area of talum treated with a 40% aqueous solution of formic acid and calcined in an inert medium at 240°C. The $S_{\rm sp}$ of this sample does not exceed 10–15 m² g⁻¹.

When developing new catalysts and improving available catalysts, a special attention is given to their strength properties principally determining their service life. The greatest decrease (30–50%) in the mechanical strength takes place during activation of catalysts. This is due to phase transformations causing changes in their crystalline and porous structures. Our experimental data on the mechanical strength of both starting samples and samples activated in an argon stream at 180°C are given in the table.

Sample no.	c _{HCOOH} , wt %	$S_{\rm sp}$, m ² g ⁻¹ , at indicated $T_{\rm a}$, °C			P, MPa		α , %, at indicated T_{a} , °C			
		180	240	280	380	initial	at 180°C	150	160	180
1	0	100	110	120	120	29	32	0	0	0
2	5.0	145	155	120	125	35	15	5	12	50
3	10.0	5	30	65	95	60	55	5	15	80
4	15.0	25	30	70	145	73	90	5	18	100
5	20.0	20	45	95	105	100	93	7	22	100
6	25.0	45	60	105	150	105	50	10	28	100
7	30.0	45	70	100	145	58	23	10	30	100
8	40.0	90	100	155	120	42	8	12	32	100
9	50.0	85	95	95	90	30	3	15	35	100
10	60.0	110	100	100	80	28	2	15	35	100

Specific surface area S_{sp} of samples, their mechanical strength P, and degree of oxygen conversion α at various activation temperatures T_a in argon stream

The catalytic activity in oxygen hydrogenation was determined at a space velocity of 6500 h⁻¹. The working gas mixture contained 2.0 vol % O₂, 6.0 vol % N_2 , and the remainder Ar. The catalytic activity of the samples was judged from the degree of oxygen conversion (see table). Prior to the experiments, the samples were activated at 150, 160, and 180°C for 1 h in an argon stream at $W = 6500 \text{ h}^{-1}$. It is seen that, as the concentration of formic acid increases, the catalytic activity (after activation at 150 and 160°C) monotonically increases and reaches a maximum for sample nos. 8-10. The increase in the activation temperature to 180°C sharply increases the catalytic activity, and sample no. 4 ensures almost 100% oxygen conversion. Under these activation conditions, however, sample no. 1 still exhibits zero catalytic activity.

We also tested the catalytic properties of sample nos. 4-7, activated under similar conditions, in the course of carbon monoxide hydrogenation. The experiments were carried out at a pressure of 3.0 MPa, space velocity of 30 000 h⁻¹, and carbon monoxide concentration at the reactor inlet of 0.6-0.75 vol %. We evaluated the catalytic activity in this process by the temperature of the 10 ppm CO breakthrough and found that sample nos. 6 and 7 have the maximal activity (220 and 215°C, respectively). These data indicate high catalytic performance of the system under study. Based on the experimental data, we chose for practical applications a catalyst with the composition 10 wt % CuO-25 wt % NiO-65 wt % talum prepared using 20% aqueous solution of formic acid in the stage of mixing.

We have studied in detail variation of the phase

composition of this sample on its heating in air and argon flows, using a GPVT-1500 high-temperature X-ray camera. The phase composition of the initial catalyst sample includes Ni(II) subcarbonate, Ni(II) and Cu(II) subaluminates, mixed Ni(II) and Cu(II) subaluminoformate, Ni(II), Cu(II), Al(III), and Ca(II) formates, and also CuO, CA, and CA₂ phases. The heating to 100°C results in the decomposition of mixed Ni(II) and Cu(II) subaluminoformate to mixed Ni(II) and Cu(II) subaluminate. This phase transformation results in a considerable increase in the intensity of reflections of mixed Ni(II) and Cu(II) subaluminate in the X-ray pattern. The heating to 175°C promotes partial decomposition of formates. At the same temperature, Ni(II) and Cu(II) subaluminates start to decompose with the removal of interlayer water, as indicated by the shift of the SA-I lines to larger angles (d = 7.2 Å). The heating to 200°C induces further SA-I decomposition with the shift of the interplanar spacing to d = 6.9 Å. The decomposition of Ni(II), Cu(II), and Al(III) formates is complete at 250°C and yields nickel and copper, which are converted to NiO and CuO in this oxidizing medium. The thermolysis of aluminum formate yields γ -Al₂O₃. The X-ray pattern contains only reflections of Ca(II) formate. The decomposition of SA-I also continues, its interplanar spacing decreases in this case to d =6.7 Å. At 300°C, calcium(II) formate starts to decompose to give CaCO₃, whereas the decomposition of SA-I approaches completion. Its interplanar spacing dbecomes equal to 6.2 Å. The intensity of diffraction reflections of this phase in the X-ray pattern considerably decreases. The further temperature increase by 50°C results in complete decomposition of calcium formate, as indicated by an increase in the intensity of $CaCO_3$ reflections. Mixed Ni(II) and Cu(II) subaluminate also completely decomposes. Nickel subcarbonate starts to decompose intensively to form finely dispersed nickel oxide. At 400°C, its decomposition is complete. The phase composition of the catalyst after thermolysis at this temperature includes the following compounds: NiO, CuO, CaO · 2Al₂O₃, CaO · Al₂O₃, and CaCO₃. The phase composition remains unchanged on cooling to ambient temperature.

The evolution of the phase composition of this sample on heating in an argon stream is almost identical, except for the fact that the dispersed Ni and Cu phases originating from the decomposition of Ni(II) and Cu(II) formates are not oxidized.

The studies of phase composition and phase transformations occurring on heating in both air and inert gas streams, of the activation stage, and also of changes in the specific surface area and mechanical strength allow us to make a substantiated choice of the scheme of the catalyst preparation. According to this scheme, the catalyst should be prepared as follows. The initial components (NSC, CSC, and talum) are mixed in the presence of 15-20% aqueous HCOOH in mixers equipped with heaters. The mixing occurs most intensively at 70-75°C. The catalyst mass with 15-20% moisture content is dried at 100-110°C in rack dryers, then crushed, mixed with graphite, and molded either as cylindrical pellets or as rings with external diameter of 10-15 mm and height not greater than 10 mm. The prepared catalyst is loaded in a reactor and activated in a stream of an inert or working gas at 180-280°C.

The experimental batch of the catalyst² in amount of 300 kg was tested in deoxygenation of electrolytic hydrogen.³ The catalyst was activated in a working gas stream (hydrogen + 0.5 vol % O_2) at 180°C, which is lower by 100–120°C than the activation temperature of NKO-2-3 catalyst used in this process. The time of attaining the working conditions was reduced by 12–15 h. The residual oxygen content in the purified hydrogen did not exceed 0.002– 0.005 vol % [24].

CONCLUSIONS

(1) The evolution of the phase composition of cement-containing nickel–copper catalysts synthesized

using aqueous formic acid involves the formation of both mixed nickel copper subaluminate and mixed nickel copper subaluminoformate, and also of nickel, copper, aluminum, and calcium formates. The quantitative ratio of these phases depends on the concentration of the aqueous solution of formic acid used.

(2) The mutual influence of metal formates on their decomposition temperature was established.

(3) The optimal concentration of formic acid aqueous solution was chosen, which allowed preparation of mechanically strong and highly active catalysts.

(4) The scheme of catalyst production taking into account basic parameters of the preparation process was offered.

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² Manufactured in Novomoskovsk Institute of Nitrogen Industry on industrial equipment for production of catalysts.

³ The tests were carried out in electrolysis shop 2 of the Azot Joint-Stock Company, Novomoskovsk.

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