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Preparation and Formation of Nickel–Copper Catalytic Systems on Various Supports and Commercial Catalysts Based on These Systems[1]

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Abstract—Based on the Ni–Cu system, catalysts were developed for low- and high-temperature industrial gas and waste gas purification. It was found that, regardless of the preparation procedure, the formation of a catalytically active structure occurred via the formation of a Ni–Cu solid solution at the stage of activation. The catalytic, physicochemical, and physicomechanical properties of NKO Ni–Cu catalysts can be purposefully regulated by changing the nature and concentration of a liquid reagent. A promoting effect of copper on the activation process and on the catalytic activity of a nickel catalytic system was found. The catalysts developed were commercialized. The catalysts were introduced into various processes of industrial gas and waste gas purification.

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INTRODUCTION

About 200–250 commercial catalysts, which are renewed at regular intervals of around five to six years, are used in chemical, petrochemical, metallurgical, and other industries in the Russian Federation [1, 2]. Catalysts whose active components are precious metals, in particular, platinum and palladium, are highly efficient in various industrial gas and waste gas purification processes. Platinum and palladium catalysts exhibit unique catalytic properties, which are responsible for their use in various catalytic processes. Both published data and industrial operating experience indicate that these catalysts are superior to all of the well-known catalysts used in organic and inorganic chemistry in activity. The best domestic catalysts from this series are PK, APK, ShPAK, etc. As a rule, they are prepared by supporting an active component from a salt solution onto a carrier; active aluminum oxide is used as the carrier. Because of the deficiency and expensiveness of these catalysts, as well as inadequate thermal stability and irreparable losses in the course of operation, the search for and the development of catalysts free of precious metals are of considerable current interest.

The practical implementation of the catalytic purification of process and waste gases is based on the use of highly efficient catalysts. The development of these catalysts is a complicated problem because, along with high activity and selectivity, they should have high mechanical strength and thermal stability, a developed geometric surface, and resistance to corrosive media and provide adequate heat removal. The following conditions are required for the development of a new catalyst:

- an available and inexpensive support with high mechanical strength and thermal stability and a developed surface, which is necessary for the stabilization of active components in a highly dispersed state;
- an active component responsible for high activity and selectivity;
- the catalyst should be thermally stable, mechanically strong, and inexpensive.

An analysis of published data indicates that nickel–copper catalytic systems can be of prime interest from the standpoint of the replacement of platinum group catalysts. These compositions were chosen as active catalyst components for the following reasons:

- the high catalytic activity of nickel and copper, as compared with other base metals, in redox processes;
- the formation of Ni–Cu solid solutions, which are responsible for high activity [3] and thermal stability and can resist oxidizing media at high temperatures [4], in the course of catalyst preparation;
- the promoting effect of copper on the reduction of nickel in nickel–copper catalysts;
- the availability of and no deficiency in raw materials for the preparation of catalysts;
- the use of preparation procedures based on low-waste technologies;
- the inexpensiveness, as compared with platinum group catalysts.

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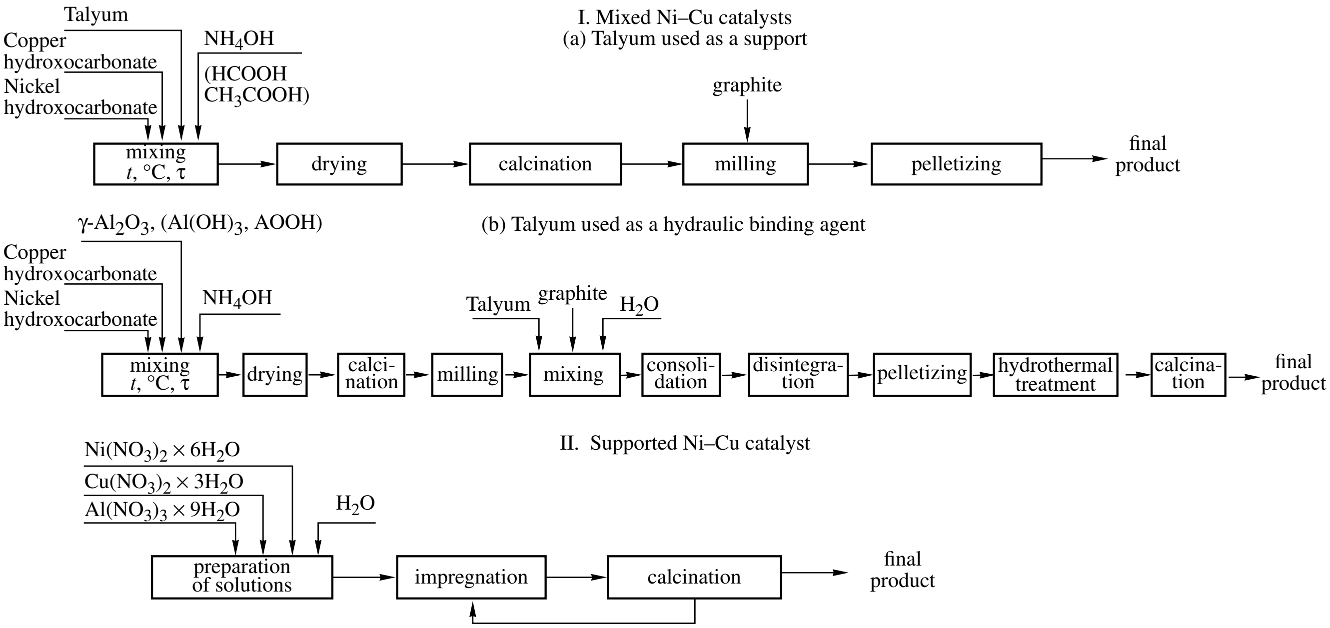

Fig. 1. Schematic diagrams of Ni–Cu catalyst preparation processes.

Various procedures for the preparation of Ni–Cu catalysts are well known [5–11]. These are mainly the supporting of active components by impregnation, the mixing of active components with a support, the coprecipitation of components, and melting followed by leaching.

In the development of a Ni–Cu catalyst for operations in both low-temperature and high-temperature processes, the following two preparation procedures were chosen: the chemical mixing of raw components in the presence of various liquid reagents and the impregnation of a support treated at a high temperature (1450–1500°C) with aqueous solutions of the salts of active components.

Figure 1 shows the schematic diagrams of catalyst preparation.

I. Ni–Cu MIXED CATALYSTS

Ni–Cu–Commercial Calcium Aluminate Catalytic System

Nickel hydroxocarbonate; copper hydroxocarbonate; commercial calcium aluminate (Talyum), which is a mixture of calcium monoaluminate (CA) and calcium dialuminate (CA_2); and an aqueous ammonia solution served as parent substances for catalyst sample preparation. In the course of preparation, the starting powder components were loaded into a heated mixer in certain ratios, and aqueous ammonia was added so that the concentration ratio between the liquid and solid phases was 1 : 1–2 : 1. The mixture was stirred with heating to a moisture content of 20–25%, unloaded, dried, calcined, ground, and pelletized.

The Draper-Lawrence simplex lattice design [12], in which all of the experimental points lay within a simplex, was used in optimizing the composition in order to reduce the number of experiments. To improve the accuracy of search, we chose the NiO–CuO–Talyum concentration ranges of 50–50–100%, respectively. We assumed that the response surface is adequately described by a third-order polynomial. In accordance with the design, samples were prepared and their properties were characterized. Based on the experimental data, regression equations were set up and tabulated using a computer, and composition–property diagrams were constructed on this basis. These diagrams allow the conditional extremum to be solved in order to determine an optimum composition. As can be seen in Fig. 2, the 0.25NiO–0.1CuO–0.65Talyum catalyst exhibited the optimum values of the test characteristics (P = 0.57 MPa, P_0 = 6.1 MPa, S_{sp} = 100 m^2/g, and A = 40°C).

The preparation conditions were optimized using a step-by-step reflection method. Catalytic activity was the optimization criterion. A sample prepared under the following conditions exhibited the highest activity in oxygen hydrogenation: mixing time of the parent components, 90 min; mixing temperature, 70–75°C; concentration of an aqueous ammonia solution, 20–25 wt %; liquid-to-solid ratio in the course of mixing, 1 : 1.

At the stage of mixing nickel hydroxocarbonate and copper hydroxocarbonate with Talyum in the presence of 25% aqueous ammonia, a chemical reaction between these components occurred with the formation of a mixed nickel and copper hydroxoaluminate, aluminum

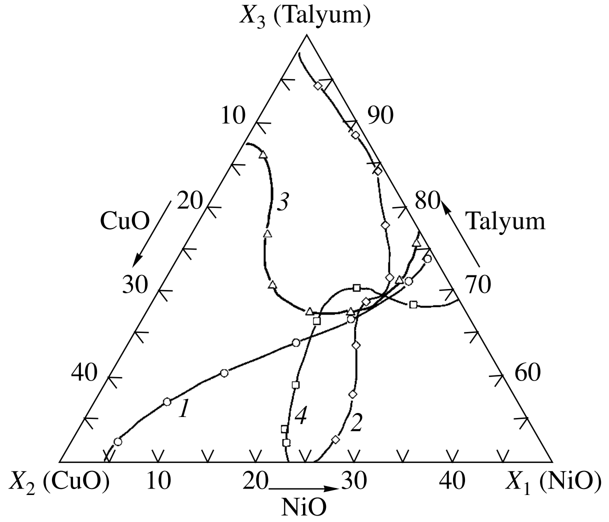

Fig. 2. Composition–property diagram for the Ni–Cu–AL–Ca catalyst. Isolines: (*1*) $P_{\square}$ = 57 MPa (pellet crush strength under end load), (*2*) P_0 = 6.1 MPa (pellet crush strength under edge load), (*3*) S_{sp} = 100 m^2/g, and (*4*) A = 40°C (catalytic activity: the breakthrough temperature of 0.01 vol % O_2 in the course of hydrogenation).

hydroxide (gibbsite), and $CaCO_3$ in two modifications (aragonite and calcite), which were identified using X-ray diffraction. The dried sample also contained minor amounts of unreacted CA_2 and dispersed nickel hydroxocarbonate and copper hydroxocarbonate.

The results of studies on phase transitions in the course of the formation of single-component (nickel hydroxocarbonate or copper hydroxocarbonate) and binary systems (nickel hydroxocarbonate–Talyum and copper hydroxocarbonate–Talyum) [13, 14] allowed us to draw the conclusions given below.

The decomposition of nickel hydroxocarbonate treated with an aqueous ammonia solution occurs in two steps. At 140°C, unbound water is removed, whereas bound water is released and CO_2 is removed in the region 300–320°C. The product of nickel hydroxocarbonate decomposition is NiO, which is reduced with hydrogen in the temperature range 200–300°C. The crystal size of nickel metal is 25 nm [13].

An ammonia–water complex of copper was formed after the treatment of copper hydroxocarbonate with aqueous ammonia at 30–50°C. An increase in the treatment temperature to 70°C facilitated the decomposition of this compound with the formation of finely dispersed copper oxide. The thermogram contained a single peak with a characteristic temperature of 320°C, which corresponds to the decomposition of copper hydroxocarbonate to CuO [14].

It was found [15] that the exchange reactions of nickel hydroxocarbonate and copper hydroxocarbonate with Talyum occur by one mechanism, which involves the formation of calcium carbonate, nickel hydroxoaluminate, and copper hydroxoaluminate.

$$\begin{gathered}CuCO_3 \cdot Cu(OH)_2 + CaAl_2O_4 + CaAl_4O_7 \\ \xrightarrow{NH_4OH} Cu_3[Al(OH)_6]_2 + Cu_3[Al(OH)_4CO_3]_2 \\ + Al(OH)_3 + CaCO_3;\end{gathered} \tag{I}$$

$$\begin{gathered}NiCO_3 \cdot 2Ni(OH)_2 + CaAl_2O_4 + CaAl_4O_7 \\ \xrightarrow{NH_4OH} Ni_3[Al(OH)_6]_2 + Ni_3[Al(OH)_4CO_3]_2 \\ + Al(OH)_3 + CaCO_3.\end{gathered} \tag{II}$$

The formation of Ni–Al–Ca and Cu–Al–Ca catalysts at the stage of calcination was accompanied by the thermolysis of nickel hydroxoaluminate and copper hydroxoaluminate to stoichiometric spinels. In this case, the excess metal oxide was released as an individual phase. In addition to $MO–Al_2O_3$ solid solutions, $M_1O–M_2O$ compounds, which are responsible for high catalytic activity, can be formed in polymetallic catalysts.

In this context, it is of interest to examine the formation of nickel–copper solid solutions in the NiO–CuO catalytic system. To eliminate the effect of the support on the formation of NiO–CuO solid solutions, we used the samples of a nickel–copper binary system, which were prepared by mechanically mixing nickel hydroxocarbonate with copper hydroxocarbonate, as well as by a technology analogous to that of catalyst preparation, as test materials. The nickel and copper contents were varied from 0 to 100 wt %. With the use of thermal analysis and X-ray diffraction, we found that a compound was formed at the stage of mixing the initial components in an aqueous ammonia solution. This compound was structurally different from nickel hydroxocarbonate and copper hydroxocarbonate. It is likely that this compound was a mixed nickel and copper hydroxocarbonate, which was formed by the following reaction:

$$\begin{gathered}CuCO_3 \cdot Cu(OH)_2 + NiCO_3 \cdot 2Ni(OH)_2 \\ \xrightarrow{NH_4OH} Cu_aNi_b(OH)_cCO_{3d}.\end{gathered} \tag{III}$$

The phase composition of the mechanical mixtures remained unchanged upon mixing.

At the stage of thermal treatment (400°C) of the test samples, the thermolysis of mixed nickel and copper hydroxocarbonate, nickel hydroxocarbonate, and copper hydroxocarbonate to nickel and copper oxides, respectively, occurred. The thermolysis of mixed nickel and copper hydroxocarbonate is characterized by lower temperatures of the removal of H_2O and CO_2 than the formation of oxides from parent nickel hydroxocarbonate and copper hydroxocarbonate. Figure 3 shows the results of the calculation of the NiO unit-cell parameter in the samples. It can be seen that, in the binary system, the NiO unit-cell parameter differed from the tabulated value (a_0 = 0.4177 nm). The NiO unit-cell parameter linearly increased with the CuO content in both the samples prepared by mechanically mixing and the sam-

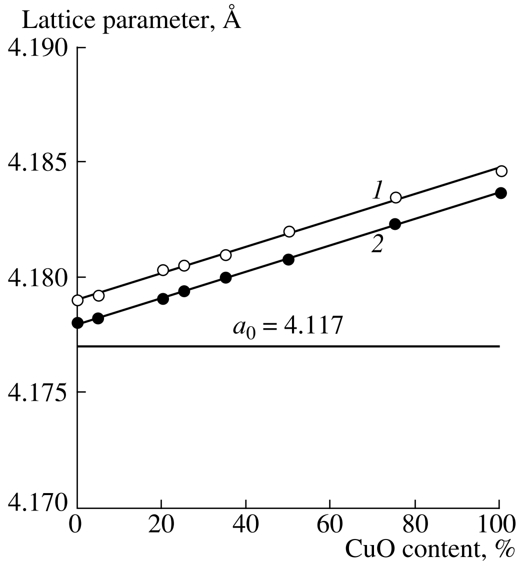

Fig. 3. Dependence of the NiO unit-cell parameter on the CuO content of the NiO–CuO binary system for samples calcined at 400°C: (*1*) mechanical mixtures and (*2*) wet mixing; a_0 is a tabulated value.

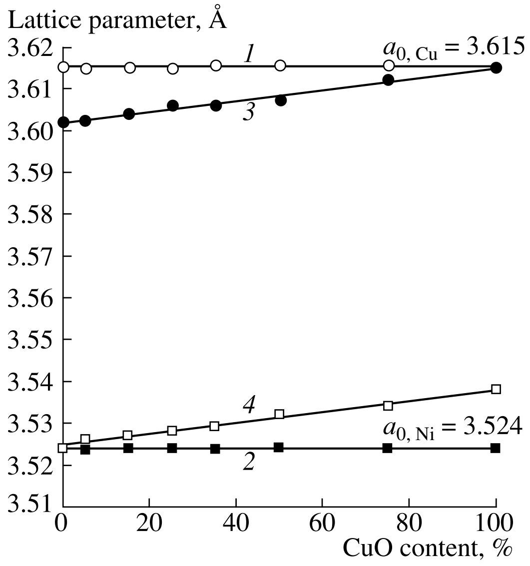

Fig. 4. Dependence of the (*1*, *3*) Cu and (*2*, *4*) Ni unit-cell parameters on the CuO content of reduced samples: (*1*, *2*) mechanical mixtures and (*3*, *4*) wet mixing.

ples treated with aqueous ammonia. This fact is indicative of the formation of a NiO–CuO solid solution based on NiO. In the case of the samples prepared by mechanical mixing, this solution was formed by the replacement of NiO at its lattice sites by mobile CuO particles upon high-temperature treatment; this is consistent with published data [16]. In the former case, its formation was due to the thermolysis of mixed nickel and copper hydroxocarbonate.

Another behavior was observed for the samples activated with hydrogen at 350°C. In both cases, the phase composition was identical and represented by Ni and Cu phases. However, the unit-cell parameters of nickel and copper in the samples treated with an aqueous ammonia solution (Fig. 4, curves *3* and *4*) were different from tabulated values and linearly changed over the entire test range of Ni and Cu concentrations. This fact suggests that a Ni–Cu solid solution, whose precursor is the thermolysis product of mixed nickel and copper hydroxocarbonate, is formed based on both Ni and Cu lattices. In the reduction of samples prepared by mechanical mixing, a Ni–Cu solid solution was not formed; this was likely due to a structural ordering in the NiO lattice in the course of NiO reduction to Ni.

Thermal and chromatographic analyses of the activation process indicated that the introduction of copper promoted the reduction of NiO in the binary system and decreased the temperature of NiO activation by more than 100°C. It was found that the maximum amount of hydrogen was consumed in the reduction of NiO and CuO formed from parent nickel hydroxocarbonate and copper hydroxocarbonate, whereas a minimum amount was consumed in the activation of samples containing 25–75 wt % CuO. This was due to the formation of xNiO · yCuO nonstoichiometric solid solutions at the stage of calcination in an atmosphere of air in samples treated with an aqueous ammonia solution. This was supported by a comparison between the theoretical and experimental amounts of oxygen contained in the test samples. The experimental amount of oxygen, which was calculated from the amount of water released upon temperature-programmed reduction with hydrogen, in samples with copper oxide concentrations of 20–80% was 0.15–0.20 kg O_2 (kg catalyst)$^{-1}$. At the same time, the theoretical oxygen content of these samples was at a level of 0.90–1.00 kg O_2 (kg catalyst)$^{-1}$. Comparing published data [17] and the experimental results, we can state that $Ni_xCu_{1-x}O_{1-y}$ solid solutions were formed at the stage of calcination in the region of intermediate compositions. After reduction, these solid solutions were converted into Ni–Cu solid solutions.

Samples containing 40–75% CuO exhibited the highest total specific surface areas of Ni and Cu (15–20 m^2/g). These catalysts exhibited the highest activity in the hydrogenation of oxygen: the temperature of 50% O_2 conversion was 60–70°C. Moreover, note that the catalytic properties of the resulting solid solution were better than analogous properties of nickel hydroxocarbonate and copper hydroxocarbonate thermolysis products.

The main properties of a Ni–Cu–Al–Ca catalyst essentially depend on preparation conditions, in particular, the concentration of a liquid reagent. Table 1 summarizes the main characteristics of samples with an optimum composition, which were prepared using aqueous ammonia solutions with different concentrations. With the use of a set of physicochemical tech-

Table 1. Effect of the concentration of an aqueous ammonia solution on the properties of catalysts

Sample no.	$[NH_4OH]$, wt %	S_{sp}, m^2/g	Mechanical strength, MPa	$[CaCO_3]$, wt %	a_0, Å		L*, Å		A, °C		ΔT, °C
					Ni	Cu	Ni	Cu	before overheating, 900°C	after overheating	
1	0	195	50	18.3	3.524	3.616	150	530	29	60	40
2	5.0	170	44	16.5	3.524	3.612	90	185	35	70	35
3	10.0	160	35	15.2	3.525	–	70	–	45	80	35
4	15.0	175	37	14.5	3.541	–	65	–	65	85	20
5	25.0	165	34	11.8	3.543	–	65	–	95	110	15

* L is the extent of dispersion.

niques, it was found that, in the course of preparation, a chemical reaction occurred between the parent components to form two modifications of $CaCO_3$ (aragonite and calcite) and mixed nickel and copper hydroxoaluminate. Unreacted CA_2 and gibbsite (a Talyum reaction product) were present in all of the samples. Moreover, a CuO phase was detected in sample no. 1, which was prepared with the use of water. Note that the interaction between nickel hydroxocarbonate and copper hydroxocarbonate with Talyum in water and an aqueous ammonia solution occurs by different mechanisms; this can be explained by different solubilities of the reagents in water and aqueous ammonia [13, 14, 18]. Mixed nickel and copper hydroxoaluminate is formed in aqueous ammonia; in this case, its concentration increased with ammonia concentration and reached maximum values in samples 3–5. In an aqueous solution, mixed nickel and copper hydroxoaluminate is formed via the formation of CuO and nickel hydroaluminate, which is structurally similar to nickel hydroxocarbonate.

This significant difference in the phase composition and structure of the resulting products is a crucial factor in the subsequent formation of the system at the stages of calcination and activation. As a result of the thermal decomposition of mixed nickel and copper hydroxoaluminate, mixed nickel and copper aluminate was formed. In calcined sample no. 1, copper occurred as copper oxide and nickel formed a nonstoichiometric spinel with aluminum. A decrease in S_{sp} was due to an increase in the fraction of unreacted CA_2. The use of Talyum as a support resulted in the formation of a mechanically strong catalyst structure. It is likely that a decrease in the strength was due to a decrease in the concentration of $CaCO_3$, which facilitates the strengthening of contacts between particles in the course of plastic deformation under compression [13].

Sample no. 5, which was calcined at 400°C, consisted of mixed nickel and copper hydroxoaluminate, NiO, NiO–CuO solid solution, boehmite, calcite, and γ-Al_2O_3 phases.

The reduction of the samples with hydrogen occurred in several steps. The thermoanalytical maximum at 160–180°C corresponded to the reduction of copper-containing oxide phases to copper metal, whose reflections were present only in the X-ray diffraction patterns of samples 1 and 2. The nickel-containing phases were characterized by two-step reduction with maximum temperatures of 300–320 and 440–460°C. An elevated activation temperature of nickel-containing phases suggests a strong bond of nickel with aluminum.

X-ray diffraction data allowed us to find that the use of water as a liquid reagent resulted in the formation of individual Ni and Cu phases, whose lattice parameters were close to tabulated values, at the stage of reduction. In the reduction of samples prepared in an aqueous ammonia solution, Ni–Cu solid solutions were formed, which are characterized by reflections that occupy intermediate positions between the reflections from Ni and Cu. It was found that, in sample nos. 2 and 3, the Ni–Cu solid solution was formed based on both Ni and Cu lattices or mainly based on the nickel lattice at concentrations of an aqueous NH_4OH solution higher than 15%. Undoubtedly, the formation of the Ni–Cu solid solution reflects the deep interaction of nickel hydroxocarbonate and copper hydroxocarbonate with Talyum in an aqueous ammonia solution with the formation of mixed nickel and copper hydroxoaluminate as an active phase precursor.

At 380°C, the decomposition of $CaCO_3$ began in sample nos. 2–5; this decomposition was complete at 450°C. The main activation process occurred over the temperature range 380–510°C. This temperature range corresponds to the reduction of nickel and copper from mixed nickel and copper hydroxoaluminate with the formation of the Ni–Cu solid solution, a maximum concentration of which was observed at 510°C. In the region 445–560°C, boehmite underwent dehydration to γ-Al_2O_3. The catalyst reduced at 600°C exhibited the following phase composition: a Ni–Cu solid solution, γ-Al_2O_3, CaO, and CA_2. The dispersity of the Ni–Cu solid solution in sample nos. 4 and 5 activated at 600°C varied over a range of 55–75. The extent of dispersion (L) of Ni–Cu solid solutions in these samples activated at 700 and 900°C was 75–80 and 100–195 Å, respectively. The test samples were characterized by a high extent of dispersion of the active components, which was especially pronounced in a Ni–Cu solid solution based on the nickel lattice.

Data on catalytic activity (*A*), which was evaluated by the temperature of 50% oxygen conversion, suggest (Table 1) that the formation of a Ni–Cu solid solution facilitates a decrease in the catalytic activity, however, at the same time, increases the thermal stability (Δt) of the system. Analogous results were obtained in a study of activity in the course of hydrogenation of carbon oxides.

The catalysts prepared using an aqueous ammonia technology and water as a liquid reagent were designated NKO-2-1 and NKO-2-2, respectively. The NKO-2-1 catalyst, which had high thermal stability characteristics, was recommended for use in high-temperature processes, whereas the NKO-2-2 catalyst was recommended for low-temperature processes.

The low-temperature decomposition of calcium carbonate in a reducing atmosphere is of crucial importance from both theoretical and practical standpoints. According to DTA data, $CaCO_3$ decomposed at 750–800°C in the test catalysts. We hypothesized that a decrease in the decomposition temperature of calcite in the reduction of aluminum–calcium-based catalysts was due to the catalytic effect of the metal (an active component of the catalyst). Moreover, the intensity of this process depended on the nature and extent of dispersion of the active component.

Table 2 summarizes the results of a study of the decomposition of calcite in NKO-2-1 (sample no. 1) and NKO-2-2 (sample no. 2) catalysts and mechanical mixtures analogous to the test catalysts in composition but different in the dispersity of nickel and copper. The reduction was performed at 400°C in a flow of hydrogen at $W = 2000$ h^{-1} for 5 h. The experimental results suggest that calcite decomposition, which occurs in the reduction of both catalysts and model mechanical mixtures like $NiO–CuO–Al_2O_3–CaCO_3$, mainly depends on the crystal sizes of nickel and copper.

We experimentally found that, at a NiO content of 0.5%, the degree of calcite decomposition was 20%, whereas 100% decomposition was reached under these activation conditions at a 30% concentration of NiO. An insignificant degree of calcite decomposition in the copper-containing system was explained by the fact that, under these conditions, the copper component underwent recrystallization and had almost no catalytic effect on this process.

Table 2. Effect of the extent of dispersion of nickel and copper on the decomposition of calcite in flowing hydrogen

Sample no.	Particle size, Å			Degree of calcite decomposition, %
	Ni	Cu	$CaCO_3$	
1	40	–	380	100
2	75	90	400	100
3	180	285	2000	55
4	1400	280	2000	10
5	190	2000	2000	30
6	1400	2000	2000	0

Note: Experimental conditions: $W = 2000$ h^{-1}; 400°C; $\tau = 5$ h.

It is well known [19–21] that activated hydrogen (H^+), which exhibits extremely high reactivity, can migrate over the surface of the M(MO)–support catalytic system or an analogous mechanical mixture. As reported, the migration of activated hydrogen molecules and atoms from active centers to the support can occur at a distance of 1–2 mm in accordance with the scheme proposed by Dalmon et al. [21]. To evaluate the probability that activated hydrogen will affect the decomposition of calcite under conditions of a reducing atmosphere, we performed an experiment in accordance with a procedure illustrated by Fig. 5. The decomposition of calcite occurred only in experiments (b) and (c). The degree of $CaCO_3$ decomposition decreased as the distance (*h*) between the active component bed and calcite was increased from 1 to 3 mm. Data obtained in this experiment indicate that the migration of activated hydrogen (spillover effect), which weakens the $CaO–CO_2$ bond and initiates the onset of this process, had a crucial effect on $CaCO_3$ decomposition.

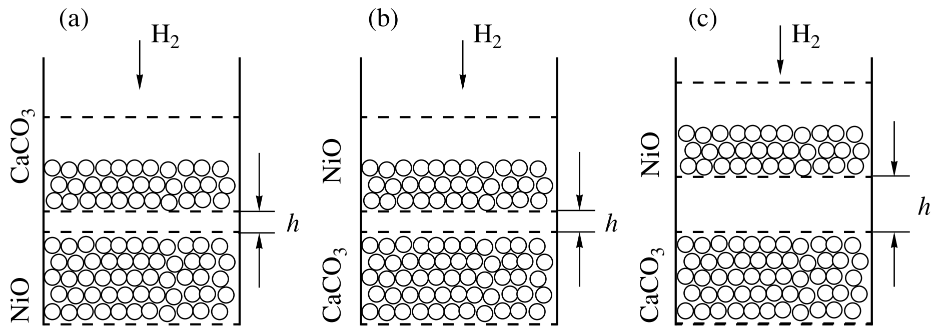

Fig. 5. Fragments of an experiment on the effect of activated hydrogen (H) on the decomposition of calcite ($W = 2000$ h^{-1}; $T = 400$°C; 5 h). h = (a, b) 1 or (c) 3 mm.

Table 3. Characteristics of NKO-2-1 and NKO-2-2 catalysts prepared using industrial equipment for catalyst manufacture at the Novomoskovsk Institute of Nitrogen Industry

Batch no.	Batch weight	Chemical composition, wt %					γ, kg/dm^3	$P_\square$, MPa	S_{sp}, m^2/g	A, %	T, °C
		NiO	CuO	CaO	Al_2O_3	calcination losses					
NKO-2-1		Technical specifications TU 113-03-31-39-85									
		27 ± 4	10 ± 2	15 ± 3	46 ± 4	no higher than 20	1.2 ± 0.1	25 ± 5	No less than		
									100	50	800
1*	600	25.9	11.4	13.1	46.8	18.6	1.2	27	120	55	810
2*	500	26.2	9.9	14.8	47.2	13.7	1.1	29	110	57	820
3	300	25.3	1.7	16.6	45.8	19.1	1.2	25	115	92	820
NKO-2-2		Technical specifications TU 113-03-31-39-85									
		27 ± 4	10 ± 2	15 ± 3	46 ± 4	no higher than 20	1.2 ± 0.1	30 ± 5	No less than		
									130	60	700
1*	800	30.4	9.8	17.1	41.2	14.6	1.2	31	145	98	730
2	300	27.3	1.2	17.2	42.5	17.8	1.1	33	135	91	730
3	250	24.4	12.0	16.3	41.9	15.0	1.3	34	150	94	720

Note: $P_\square$ is the mechanical crushing strength of pellets under end load; A is the conversion of O_2 reached at 150°C; and T is thermal stability (the temperature of overheating after which the activity remained unchanged).

The results obtained in the development of mixed nickel–copper–aluminum–calcium catalysts were used in the pilot-scale production of these catalysts. In this case, the reproducibility of the main performance characteristics of NKO-2-1 and NKO-2-2 catalysts was tested. The samples were prepared using the available industrial equipment for catalyst manufacture at the Novomoskovsk Institute of Nitrogen Industry. It was found that the industrial use of the recommended preparation procedure afforded highly reproducible catalysts with the use of various mixing and calcination equipment (Table 3). The manufacturing process parameters were determined, and technical specifications were developed.

The NKO-2-1 catalyst was industrially tested in an ART-0.75 system for the two-step removal of oxygen from argon at Novolipetsk Steel (NLMK) in order to replace a PK-1 platinum catalyst. The residual oxygen content of purified argon was no higher than 5 ppm. In addition, the NKO-2-1 catalyst was introduced in a system for the production of a protective atmosphere at the PO Pishmash in Kirovograd. At a temperature of 130–150°C in the purification reactor, the residual oxygen content was no higher than 5 ppm and corresponded to a regulated value. During the operating period, high strength and thermal stability characteristics of the catalyst were confirmed.

The NKO-2-2 catalyst, which has a lower activation temperature, was introduced in a system for the drying and purification of electrolytic hydrogen in order to remove oxygen impurities at the Azot Joint Stock Company in Novomoskovsk (Elektroliz-2 Department). It was noted that the activity of the introduced catalyst was higher than that of a Ni–Cr catalyst.

The NKO catalysts should be reduced with a hydrogen-containing gas at 350–450°C before use. In a number of cases, it is difficult to produce these temperature conditions in available systems. An analysis of published data on the use of carboxylate salts and carboxylic acids as liquid reagents in catalyst technologies suggests that supports and highly efficient catalysts can be prepared; the activation of these catalysts is performed in a low-temperature region (150–250°C) in a flow of inert gases.

This preparation procedure is based on the fact that the thermolysis of carboxylate salts in an inert atmosphere occurs with the formation of metals [22]. The synthesis of samples was performed by mixing parent raw components in the presence of an aqueous solution of formic acid, whose concentration was varied over the range 5.0–60.0 wt % (Table 4). The mixing was performed at 60–80°C and a liquid-to-solid ratio of 1 : 1–1.5 : 1. The catalyst mass with a moisture content of 15–20% was dried at 100°C, ground, and pressed as cylindrical pellets 6.0 mm in diameter and 5.0 mm in height at a specific pressure of 650 MPa.

To understand phase-formation processes in the synthesis of nickel–copper cement-containing catalytic systems, we studied samples prepared by the treatment of nickel hydroxocarbonate, copper hydroxocarbonate, their mixture (50% nickel hydroxocarbonate + 50% copper hydroxocarbonate), active aluminum oxide,

Table 4. Dependence of the specific surface area (S_{sp}), mechanical strength ($P_{\square}$), and oxygen conversion (α) on the temperature of activation (T_{act}) in a flow of argon

Sample no.	[HCOOH], wt %	S_{sp}, m^2/g				$P_{\square}$, MPa		α, % T_{act}, °C		
		T_{act}, °C								
		180	240	280	380	initial	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

$CaCO_3$, and calcium aluminate with a 40% aqueous solution of formic acid.

An analysis of the DTA curves of the test samples indicated that the decomposition of nickel formate or copper formate occurred in two steps or as a single step, respectively. The decomposition of a mixture of Ni(II) and Cu(II) formates is characterized by two strong endothermic peaks. An endo effect with T_{max} = 180°C belongs to the decomposition of $Cu(HCOO)_2$ and the dehydration of $Ni(HCOO)_2 \cdot 2H_2O$, whereas an exo effect with T_{max} = 215°C belongs to the 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. On the other hand, under the given conditions of the treatment of a mixture of nickel hydroxocarbonate and copper hydroxocarbonate, a double formate salt of Cu(II) and Ni(II) like $CuNi(HCOO)_2 \cdot 2H_2O$ may be formed [23], and this salt can also decompose in two steps.

In the course of the preparation of nickel–copper cement-containing catalytic systems (25 wt % NiO–10 wt % CuO–65 wt % Talyum), it was found that the interaction of a mixture of the parent components (nickel hydroxocarbonate + copper hydroxocarbonate + Talyum) and aqueous formic acid at room temperature occurred at a very low rate, which reached a maximum value at 70–75°C. This is an optimum temperature for interaction between these components in the presence of aqueous formic acid, as well as for either of these individual components. Experimental data obtained with the use of complex thermal and X-ray diffraction (XRD) analysis allowed us to subdivide the samples into three groups depending on the concentration (%) of the aqueous formic acid solution used at the stage of mixing:

I no. 1, H_2O; no. 2, 5.0; no. 3, 10.0;

II no. 4, 15.0; no. 5, 20.0; no. 6, 25.0; no. 7, 30.0;

III no. 8, 40.0; no. 9, 50.0; no. 10, 60.0.

The formation of samples at the stage of mixing essentially depends on the concentration of an aqueous formic acid solution. According to XRD data, the phase composition of sample nos. 1 and 2 was practically identical. It was represented by the phases of nickel hydroxocarbonate, copper hydroxocarbonate, mixed nickel and copper hydroxoaluminate, CuO, $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, and insignificant amounts of nickel, copper, aluminum, and calcium formates. An increase in the concentration of HCOOH to 10% (sample no. 3) increased the degree of interaction between the parent components. The phase composition of sample 5 was dramatically different from the composition of previous samples: the following nickel and copper hydroxoaluminates were predominant:

(1) Standard Ni(II) and Cu(II) hydroxoaluminates (HA-I) having the main interplanar spacing d = 7.6 and 3.8 Å, respectively.

(2) Ni(II) and Cu(II) hydroxoaluminates (HA-II) different from the standard species in that the $HCOO^-$ anion is an additional constituent of their structure. They have the main interplanar spacing d = 11 and 5.5 Å, respectively.

Various anions that replace the OH^- group [21], such as CO_3^{2-}, and NO_3^-, can be the constituents of metal hydroxoaluminates. The general formula of HA-I can be written as $MAl_2(OH)_8$, where M is Ni, Cu, Zn, Mg, etc., whereas the formula of HA-II is

$MAl_2(OH)_{8-x}(HCOO)_x$ (metal hydroxoaluminoformate).

As the acid concentration was further increased to 30%, compounds like HA-II, that is, mixed Ni(II) and Cu(II) hydroxoaluminoformates, were primarily formed. Moreover, in this sample, the amount of the resulting Ni(II), Cu(II), Al(III), and Ca(II) formates increased. An amount of nickel hydroxocarbonate, CA, CA_2, CuO, and $CaCO_3$ was also present.

The phase composition of sample no. 8 was mainly formed from Ni(II), Cu(II), Al(III), and Ca(II) formates, whereas Ni(II) and Cu(II) hydroxoaluminoformates were detected only in minor amounts. The use of a 50% aqueous solution of formic acid (sample no. 9) was even more favorable for the formation of Ni(II), Cu(II), Al(III), and Ca(II) formates. A further increase in the acid concentration to 60% did not affect the phase composition. In all of the test samples, a $CaCO_3$ phase was detected as a product of the exchange interaction of nickel hydroxocarbonate and copper hydroxocarbonate with Talyum at the stage of mixing.

Activation is an important stage in the formation of a catalytically active structure. The conditions of activation are responsible for catalyst characteristics such as catalytic activity, mechanical strength, and service life.

It was found that the thermolysis of samples in a flow of an inert gas is actually the stage of activation. This is a multistep process, which occurs at 125–400°C. The test samples can be subdivided into three groups with respect to activation. The first group consists of sample nos. 2 and 3, in which the main activation process occurred at 200–400°C with a relatively low intensity. The second group (sample nos. 4 and 5) is characterized by three-step activation (130–170, 200–300, and 300–400°C). In the third group, activation occurred with a high intensity in two steps (170–190 and 215–225°C), which correspond to the decomposition of nickel and copper formates in a flow of an inert gas. Temperature-programmed activation data adequately correlate with XRD data on phase composition and with the experimental results obtained by complex thermal analysis.

Table 4 summarizes the temperature dependence of the specific surface area, the mechanical strength, and the catalytic activity in the course of oxygen hydrogenation. In sample no. 2, the products of Talyum hydration and reactions with nickel hydroxocarbonate and copper hydroxocarbonate and, in part, the decomposition products of Ni and Cu formates made the main contribution to the development of the surface, whereas the decomposition products of Ni and Cu hydroxoaluminoformates (HA-II) and formates (HA-I) formed the surface in sample nos. 4–10. In these samples, the specific surface area, which was measured on a Tsvet 211 using the thermal desorption of argon, is the total active surface of nickel and copper.

In the development of new catalysts and in the improvement of currently available catalysts, attention is focused on strength characteristics, which are primarily responsible for the service life. The greatest decrease in the mechanical strength (30–50%) took place in the course of catalyst activation. This phenomenon results from phase transformations, which change the crystal and pore structures. Table 4 summarizes the experimental results of a study of the mechanical strength of samples before and after activation in a flow of argon at 180°C. The dependence of the mechanical strength of both initial and activated samples on the concentration of formic acid exhibits a pronounced maximum at 15–25% HCOOH (sample nos. 4–6). The mechanical strength of initial samples lay in the range 73–105 MPa. After activation for 1 h, the character of the dependence remained unchanged. In this case, the maximum mechanical strength decreased to 50–93 MPa.

Note that, as the concentration of formic acid was increased under conditions of activation at 150 and 160°C, the catalytic activity increased monotonically and reached a maximum value in sample nos. 8–10. An increase in the activation temperature to 180°C facilitated a dramatic increase in the catalytic activity, and 100% oxygen conversion was detected even in the presence of sample no. 4. Under these activation conditions, sample no. 1 was inactive.

An analysis of experimental data allowed us to choose the catalyst 10 wt % CuO–25 wt % NiO–65 wt % Talyum, which was prepared with the use of a 20% aqueous solution of formic acid at the stage of mixing, for practical implementation.

The phase composition of the initial sample of this catalyst was represented by Ni(II) hydroxocarbonate; mixed Ni(II) and Cu(II) hydroxoaluminate; mixed Ni(II) and Cu(II) hydroxoaluminoformate; Ni(II), Cu(II), Al(III), and Ca(II) formates; and CuO, CA, and CA_2 phases. The formation of an active component of the catalyst was mainly complete at 250°C. The phase composition of the catalyst after thermolysis at 400°C was represented by the following compounds: Ni, Cu, and a Ni–Cu solid solution, which is a decomposition product of mixed Ni(II) and Cu(II) hydroxoaluminoformate, as well as $CaO \cdot 2Al_2O_3$, $CaO \cdot Al_2O_3$, $CaCO_3$, and γ-Al_2O_3.

The results obtained in the study of the activation stage and an analysis of data on changes in the specific surface area and mechanical strength allowed us to choose soundly a catalyst preparation procedure. According to this procedure, the catalyst should be prepared as follows: The starting raw components (nickel hydroxocarbonate, copper hydroxocarbonate, and Talyum) are mixed in the presence of a 20% aqueous solution of HCOOH in heated mixers. At the stage of mixing, the process occurs most intensely at 70–75°C. The catalyst mass with 15–20% humidity is dried at 100–110°C in rack driers; next, it is ground, mixed with

Table 5. Characteristics of supported catalyst samples

Sample no.	Chemical composition, wt % (NiO/CuO)	Initial samples						After reduction with hydrogen (600°C) in a KL-1 unit				
		$P_\square$, MPa	S_{sp}, m^2/g	phase composition	L_{Ni}, Å	J^{1000}, (2.03 Å), mm^2	J^{1000}, (2.08 Å), mm^2	phase composition	L_{Ni}, Å	$a_{o,Ni}$, Å	J^{1000}, (2.03 Å), mm^2	J^{1000}, (2.08 Å), mm^2
Support	–	58	2	CA$_6$, α-Al$_2$O$_3$, CA$_2$	–	–	–	–	–	–	–	–
1	NiO 6.0 CuO 4.8 (1.33)	93	30	CA$_6$, α-Al$_2$O$_3$, CuO, CA$_2$, NiO–CuO, CaCO$_3$	95	160	–	CA$_6$, α-Al$_2$O$_3$, Ni, CA$_2$, Cu	115	3.54	280	360
3	NiO 7.5 CuO 2.9 (2.59)	95	35	CA$_6$, α-Al$_2$O$_3$, NiO–CuO, CA$_2$	95	290	–	CA$_6$, α-Al$_2$O$_3$, Ni–Cu, CA$_2$,	115	3.54	580	30
4	NiO 8.7 CuO 2.1 (4.14)	94	40	CA$_6$, α-Al$_2$O$_3$, NiO–CuO, CA$_2$, CaCO$_3$	85	220	270	CA$_6$, α-Al$_2$O$_3$, Ni–Cu, CA$_2$	115	3.54	550	40
5	NiO 8.3 CuO 1.9 (4.37)	94	25	CA$_6$, α-Al$_2$O$_3$, NiO–CuO, CA$_2$, CaCO$_3$	110	170	1440	CA$_6$, α-Al$_2$O$_3$, Ni–Cu, CA$_2$	115	3.54	610	190
6	NiO 9.0 CuO 2.0 (4.54)	–	–	CA$_6$, α-Al$_2$O$_3$, NiO–CuO, CA$_2$	125	310	400	CA$_6$, α-Al$_2$O$_3$, Ni–Cu, CA$_2$	115	3.54	570	225
7	NiO 9.0 CuO 1.9 (4.74)	100	25	CA$_6$, α-Al$_2$O$_3$, NiO–CuO, CA$_2$	110	370	170	CA$_6$, α-Al$_2$O$_3$, Ni–Cu, CA$_2$	115	3.54	600	300

Note: The tabulated Ni lattice parameter is $a_{0,\,Ni} = 3.52$ Å.

graphite, and pelletized as either cylindrical pellets or rings with an outer diameter of 10–15 mm and no more than 10 mm in height. The prepared catalyst is loaded in a reactor and activated in a flow of an inert or working gas at 180–280°C.

A pilot batch of the catalyst (300 kg), which was prepared using the industrial equipment of catalyst manufacture at the Novomoskovsk Institute of Nitrogen Industry, was tested in the process of oxygen removal from electrolytic hydrogen at the Elektroliz-2 Department of the Azot Joint Stock Company in Novomoskovsk. The catalyst was activated in a flow of a working gas (H_2 + 0.5 vol % O_2) at 180°C, which is 100–120°C lower than the treatment temperature of an NKO-2-3 catalyst used in this process. The setup time of the system was shortened by 12–15 h. The residual oxygen concentration in purified hydrogen at 180°C was no higher than 0.002–0.005 vol %.

In the development of a Ni–Cu catalyst (with various geometric shapes, in particular, as cylindrical pellets, rings, and extrudates) with a reduced activation temperature, a preparation procedure was chosen as a result of which active components occurred in a state bound to the support. Because of this, a Ni–Cu solid solution was formed at lower temperatures than in the NKO-2-1 catalyst (Fig. 1, scheme Ib).

In this procedure, the hydraulic binding properties of Talyum were used; that is, the preparation was performed so that Talyum did not interact with nickel hydroxocarbonate and copper hydroxocarbonate. Aluminum hydroxide (gibbsite or boehmite) or γ-Al_2O_3 was used as a support. The amount of Talyum added to the catalyst mixture was equal to 40 wt %. The fraction of a support was 30 wt % on a γ-Al_2O_3 basis. The total concentration of active components was equal to 25 wt % NiO + 10 wt % CuO.

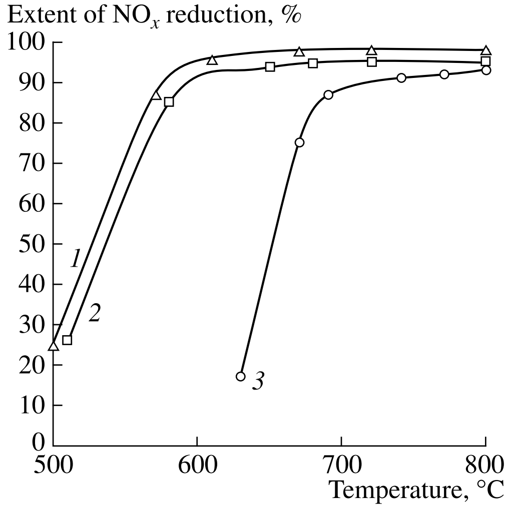

Fig. 6. Effect of treatment temperature on the extent of nitrogen oxide reduction at a ratio of NiO/CuO = 2.59. W = (*1*) 10000, (*2*) 25000, and (*3*) 50000 h^{-1}.

The formation of a catalytically active structure began at the stage of mixing nickel hydroxocarbonate and copper hydroxocarbonate with aluminum hydroxide in the presence of 25% aqueous ammonia with the formation of mixed nickel and copper hydroxoaluminate and $Ni(OH)_2$. Moreover, the phase composition was represented by gibbsite, as well as nickel hydroxocarbonate and copper hydroxocarbonate unreacted with it. According to DTA data, the unreacted nickel hydroxocarbonate and copper hydroxocarbonate formed mixed nickel and copper hydroxocarbonate. Mixed nickel and copper aluminate and a Ni–Cu solid solution were formed as a result of thermolysis. Because the amount of the support in the Ni–Cu–Al_2O_3 ternary composition was insufficient, it is evident that most of the Ni–Cu solid solution was formed at the stage of activation from the NiO–CuO solid solution, the source of which was mixed nickel and copper hydroxocarbonate.

At the stage of hydrothermal treatment, calcium monoaluminate and calcium dialuminate underwent changes in phase composition to form $3CaO \cdot Al_2O_3 \cdot 6H_2O$ as a result of hydration. Moreover, gibbsite, boehmite, and $CaCO_3$ (products of the reaction of $Ca(OH)_2$ with CO_2 dissolved in water) were formed in the course of hydration. After calcination at 400°C, the phase composition was represented by NiO, γ-Al_2O_3, $C_{12}A_7$, $CaCO_3$, CA_2, and boehmite. At the stage of hydrothermal treatment (1.5 h; 75–80°C), a mechanically strong catalyst structure was formed, which essentially depended on the conditions of Talyum hydration.

In the course of activation in hydrogen, starting at 150°C, the reduction of free CuO to Cu occurred to initiate the reduction of NiO. In the range 250–380°C, the phases of copper oxide and nickel oxide did not manifest themselves individually, and a reflection due to a Ni–Cu solid solution appeared in the diffraction pattern. At 380°C, active components were completely converted into this compound.

The catalyst prepared in accordance with this procedure was designated as NKO-2-3. The commercial production of this catalyst in both pelletized (cylindrical pellets and rings) and molded forms was implemented at the Novomoskovsk Institute of Nitrogen Industry. The catalyst successfully operated in systems for the removal of oxygen from argon, in plants for producing dilute nitric acid, in the removal of nitrogen oxides from flue gases, in the removal of hydrocarbons from the krypton–xenon fraction, etc.

II. SUPPORTED Ni–Cu CATALYSTS

The following stringent requirements are imposed on the catalysts used in catalytic treatment reactors: the catalysts should have high activity, mechanical strength, and resistance to oxidizing atmospheres, and the shape of the catalysts should provide low hydraulic resistance. A catalyst that meets these requirements can be prepared by impregnating a support that has high mechanical strength (to 50–60 MPa), water uptake of no less than 20%, and low hydraulic resistance due to a complex geometric shape with active components.

To prepare the catalyst, we used the support of the NIAP-18 catalyst for natural gas steam conversion. The final stage of the preparation of this support was high-temperature (1480–1500°C) calcination. The main phases of the support prepared were $CaO \cdot 6Al_2O_3$ (CA_6), corundum (α-Al_2O_3), and an amount of $CaO \cdot 2Al_2O_3$ (CA_2). This support had a water uptake of 27% and a mechanical strength of 50–60 MPa; it was made as rings of size 15 × 10 × 7 mm. The support was impregnated with aqueous solutions of Ni(II), Cu(II), and Al(III) nitrates.

To choose a catalyst with a maximum activity, we studied samples in which the NiO/CuO concentration ratio was varied. Three impregnations with the intermediate calcination of the samples were performed in order to reach the total concentration of Ni and Cu in the catalyst at a level of 10–12 wt %.

The temperature of catalyst calcination after impregnation (400°C) was chosen based on an analysis of the thermoanalytical curves of Ni(II), Cu(II), and Al(III) nitrates.

After impregnation, the mechanical strength increased because of the hydration of CA_2, as compared with the initial support. The mechanical strength of the calcined catalyst remained unchanged and lay at a level of 92–100 MPa over the entire test range of NiO/CuO ratios (Table 5).

According to XRD data, the phase composition of the initial catalyst samples was identical and represented by the compounds CA_6, NiO, and CA_2. The CuO phase was detected only in a sample with the ratio

Table 6. Applications of cement-containing catalysts to the purification of gas emissions and process gases

Process	Base catalysts for the preparation of modified catalysts	Working temperature range, °C	Purification efficiency	Organizations where (a) model, (b) pilot, (c) experimental industrial, and (d) commercial tests were performed
Removal of CO from flue gases by oxidation	NIAP-15-01 (NKO-2-1) NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NLO-2-3K) (TU 113-03-00209510-49-90)	250–400	To 99.9%	(a) GIAP, Grodno; INKhP, Azerbaijan; VNIIOS, Moscow; (d) PO Azot, Kemerovo
Nitrogen oxide removal from internal-combustion engine exhaust emissions by reduction	NIAP-15-01 (NKO-2-1) NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NLO-2-3K) (TU 113-03-00209510-49-90)	250–800	No more than 50 ppm	(b) SKTB Minavtotrans, Armenia; ID, Moscow; (c) Novomoskovsk Car-Repair Works; Novomoskovsk Gypsum Plant; NPO Energiya; Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences; etc.
Removal of NO_x from waste gases in the manufacture of dilute nitric acid	NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NKO-2-3K) (TU 113-03-00209510-49-90)	400–800	No more than 0.005 vol %	(c) Kirovochepetsk PO Azot, Berezniki PO Azot, and Kemerovo PO Azot; (d) Novomoskovsk AK Azot
Removal of ammonia from gases by catalytic decomposition to N_2 and H_2	NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NKO-2-3K) (TU 113-03-00209510-49-90)	650–950	No more than 0.06%	(a) IG, Ukraine; VUKhIN, Yekaterinburg; (d) Novolipetsk Steel (NLMK)
Removal of ammonia from gases (ammonia oxidation)	NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NKO-2-3K) (TU 113-03-00209510-49-90)	300–350	99.0–99.6%	(a) Novomoskovsk Institute of Nitrogen Industry
Removal of organic impurities from waste gases by deep oxidation	NIAP-15-01 (NKO-2-1) NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NLO-2-3K)	250–400	91–99%	(a) NPO Organic Intermediaries and Dyes (NIOPIK), Moscow; NIIGAZ, Dzerzhinsk
Removal of oxygen and hydrogen from gases	NIAP-15-01 (NKO-2-1) NKO-2-2 NIAP-15-02 (NKO-2-3Ts) NIAP-15-03 (NKO-2-3K) (TU 113-03-00209510-49-90)	200–750 180–700 180–750	No more than 5 ppm O_2 ″ ″	(a) GIAP; NPO Kriogenmash, Balashikha; (d) Novolipetsk Steel (NLMK); Nizhnekamskneftekhim; Pishmash, Kirovograd; NAK Azot, Novomoskovsk; Seversk Pipe Plant; etc.
Removal of hydrocarbons (CH_4 etc.) and oxygen from gases	NKO-2-3F	450–550	No more than 0.01–0.02 ppm O_2	(a) NPO Kriogenmash, Balashikha; (c) Zapsib, Novokuznetsk; AO Khrom, Murom; Mariupol Metal Works; Maili-Saisk Electric Lamp Factory

NiO/CuO = 1.33. The extent of dispersion $L_{\text{NiO–CuO}}$ lay at a level of 85–125 Å in all of the samples.

In the course of studies of the samples prepared by the given procedure, we obtained the dependence of the total concentration of active components and the mechanical strength on time, temperature, and number of impregnations. In this case, we found that the total concentration of active components in the catalyst increased. The mechanical strength somewhat decreased as the temperature and impregnation time were increased, whereas it increased by a factor of 2.5–3.0 with increasing number of impregnations. This increase in the strength can be explained in terms of the Rehbinder theory of the physicochemical mechanics of disperse solids. According to this theory, a ceramic support plays the role of a frame, whereas active components, which fill pores, play the role of a phase that withstands elastic deformations.

The reduction process occurred in three steps. At the first step (T_r = 220–230°C), CuO was reduced. The second (T_r = 300–310°C) and third (T_r = 430–450°C) steps corresponded to the reduction of free NiO and NiO bound to the support, respectively. After the reduction in hydrogen, nickel metal was detected in the phase composition of the samples. Based on XRD analysis data, the Ni lattice parameter (a_0) was calculated. It was equal to 3.54 Å for all of the samples (Table 5). A distortion in a_0 was due to the insertion of Cu atoms into the crystal lattice of Ni, as a result of which a Ni–Cu solid solution was formed.

It was found that the concentration ratio between nickel and copper had a considerable effect on the catalytic activity in nitrogen oxide reduction with methane. The dependence of the catalytic activity on the NiO/CuO ratio exhibited an extremum. An increase in the NiO/CuO ratio from 1.33 to 2.59 resulted in an increase in the activity, whereas a further increase in the ratio to 4.74 decreased the activity. An activity maximum was observed at the ratios of 2.3–3.0. It is likely that this phenomenon can be explained by the fact that a certain ratio between NiO and CuO in the range 2.3–3.0 is required for the formation of a Ni–Cu solid solution. At high temperatures of the treatment process, free Ni and Cu (which were not the constituents of a solid solution) underwent recrystallization; it is likely that the catalytic activity decreased for this reason. Nevertheless, a general regularity in changes in the catalytic activity with temperature can be noted. An increase in the catalytic activity with temperature was observed. In the range 650–800°C, the activity was almost the same in all of the samples. A maximum difference in the activity manifested itself in the region 500–650°C. The samples exhibited the highest activity in the range 750–800°C (the residual NO_x concentration in this temperature range was 0.003–0.005 vol %).

With the use of XRD analysis, we found that the samples were well reduced after the determination of the activity. The phase of nickel metal in the sample had a distorted parameter a_0, which was equal to 3.54–3.57 Å. This suggests the formation of a Ni–Cu solid solution. In a sample with a maximum activity (NiO/CuO = 2.59), the dispersity of nickel was equal to 190 Å. In this sample, we studied the effect of space velocity on the catalytic activity (Fig. 6). An increase in the space velocity by a factor of 2.5 (from 10000 to 25000 h^{-1}) affected the catalytic activity only slightly. A further increase in the space velocity by a factor of 2 (from 25000 to 50000 h^{-1}) resulted in a dramatic decrease in the activity in the temperature region 500–700°C. In the range 700–800°C, the space velocity had almost no effect on the activity. At a space velocity of 50000 h^{-1}, 100% conversion was not reached even at 800°C. The "ignition" temperature of the test samples lay in the range 600–620°C, which is somewhat higher than this value for the APK-2 alumina–palladium catalyst.

The nickel–copper catalysts differing in preparation procedure and chemical composition were tested in various processes of organic, inorganic, and environmental catalysis. Table 6 summarizes the processes in which platinum group catalysts were replaced by NKO catalysts.

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