

IV RUSSIAN CONFERENCE WITH THE PARTICIPATION OF CIS COUNTRIES ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY

Main Features of the Synthesis and Formation of Cement-Containing Catalysts for Various Processes of Organic, Inorganic, and Environmental Catalysis

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Abstract—The formation of copper-, manganese-, nickel–copper, and other cement-containing catalysts for organic, inorganic, and environmental catalysis are studied by physicochemical and physicomachanical methods. The catalysts are prepared by chemical mixing, impregnation, and mechanochemical activation with high-pressure water jets (30–300 MPa). Strong metal–support interaction during the preparation of the catalysts and the introduction of manganese compounds stabilize copper ions in oxides, hampers the reduction of oxides, and improves the thermal stability of samples and the stability to mechanical disintegration during performance. Deeper interaction between copper and zinc salts enhances the efficiency of copper catalysts. The technologies of the industrial syntheses of catalysts for various industries is developed and used.

INTRODUCTION

Oxide catalysts for many organic and inorganic processes are commonly produced by coprecipitation from solutions [1, 2]. The mixed metal hydroxycarboaluminate–chromite phase with the hydrotalcite–pyroaurite structure and the $M_x^{2+} M_y^{3+} (OH)_k (CO_3) \cdot nH_2O$ composition, where M is a metal, is often a precursor of the active state of the catalyst. This phase is characterized by a diffraction pattern with a typical set of maxima, which correspond to interplanar distances d of 7.7, 3.9, 2.6, 2.3, and 2.0 Å. Further thermal treatment at 350–400°C results in the formation of highly dispersed and structurally imperfect protospinel, which are anion-modified oxides. Their presence enhances the activity, selectivity, thermal stability, and mechanical strength of the catalysts and finally increases the durability of the catalyst performance [3–5].

The physicochemical bases for the formation of catalysts by the methods of chemical mixing and/or heterogeneous ionic exchange between metal hydroxycarbonates and high-alumina cements in water or water–ammonia media have been developed at the Novomoskovsk Institute of Nitrogen Industry together and other institutions, including the Zelinskii Institute of Organic Chemistry (Professor Yakerson and others) [6–10].

As was shown, the main product of the interaction between hydroxycarbonates of metals and calcium aluminates is the above precursor, a compound with the hydrotalcite–pyroaurite structure, or a complex salt with the structure close to that of initial hydroxycarbonate and $CaCO_3$ (calcite). A simple and environmentally safe technology for the preparation of the catalysts enables the high catalytic activity, which is provided by the formation of the active precursor. In addition, the

presence of calcium aluminates enhances significantly the mechanical strength of samples and their formability as pellets, rings, and extrudates with various sizes. Based on this technology, commercial catalysts of different types for various processes have been developed. However, improving the efficiency of cement-based catalysts, prolonging their lifetimes, extending the application areas, and broadening the range of raw materials requires further studies of the formation processes. It is necessary to continue a search of techniques providing good technological parameters (the shapes of granules, their sizes, etc.).

Interaction of Metal Basic Carbonate with High-Alumina Cements

The interaction of manganese hydroxycarbonate (MnHC) with calcium aluminates in an aqueous medium directly concerns the synthesis of manganese–aluminum–calcium catalysts for redox processes. As was shown [6–13], a process close to heterogeneous ionic exchange occurs between MHC ($M = Cu, Zn, Ni, Co$, and Mn) and calcium aluminate in an aqueous medium. MHC either retains its structure ($M = Co$ and Ni) or transforms to metal hydroxycarboaluminate ($M = Zn$ and Cu). In the synthesis of nickel-, copper-, zinc-, and other cement-containing catalytic systems, the $CaCO_3$ phase is the product of interaction and its concentration is maximal when the concentration of MO is 30–50% (Fig. 1). During preparation, MnHC was mixed with talum in an aqueous medium at 75°C and the samples obtained were dried at 100°C. The manganese concentration (based on Mn_3O_4) varied from 0 to 100%. The mechanical mixtures of initial reactants were studied in parallel [14].

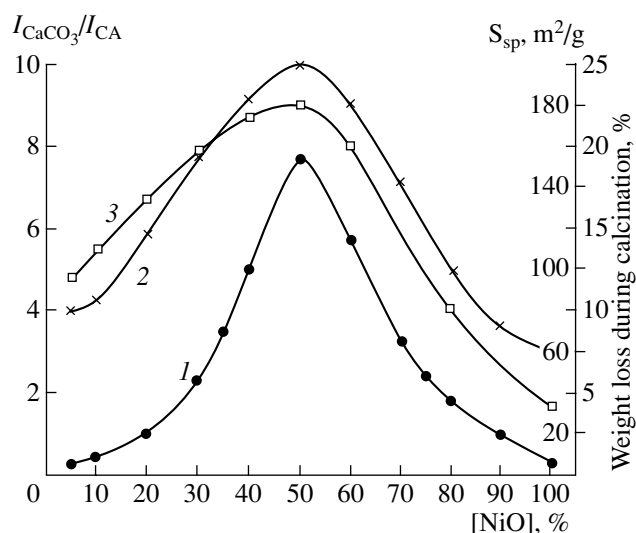


Fig. 1. (1) Weight loss during calcination, (2) specific surface area of the sample, and (3) the intensity of the line corresponding to $d = 3.03 \text{ \AA}$ (CaCO_3) relative to that of calcium monoaluminate as a function of the composition of nickel–aluminum–calcium catalyst.

As was found in the studies of other systems (nickel, copper, zinc, and cobalt), calcium carbonate calcite formed when MnHC was mixed with calcium aluminate in an aqueous medium [6, 15]. A curve for the intensity of X-ray diffraction, corresponding to an interplanar distance $d = 3.03 \text{ \AA}$, as a function of the composition passes through a maximum at a Mn_3O_4 concentration of 30–40 wt % (Fig. 2). Reflexes typical of compounds with the hydrotalcite structure are absent from diffraction patterns. However, a profile of the X-ray diffraction maxima due to MnHC differs substantially from those for mechanical mixtures. The integral intensity halves, and the lines broaden. This can be due to the release of carbonate ions from the MnHC lattice and the incorporation of aluminate and hydroxide ions, which are the products of dissolution and hydrolysis of calcium aluminates, into the voids.

The participation of aluminate ions in exchange might suggest the formation of compounds of this type. However, these compounds were not found. As was mentioned above, exchange between CO_3^{2-} and $\text{Al}(\text{OH})_4$ can occur without the reconstruction of the metal hydroxycarbonate. The formation of $\text{MO} \cdot \text{Al}_2\text{O}_3$ disordered solid solutions based on the MO lattice at 350–400°C indirectly confirms this assumption.

Calcination in air results in the formation of Mn_3O_4 and MnO_2 but the overlapping of the reflections from these oxides with those of other phases in the sample hampers the determination of the lattice parameters for manganese oxides. Therefore, thermal decomposition was carried out in an H_2 flow at 500°C. The lattice parameters for MnO formed are less than the tabulated values. The parameter of the MnO crystalline lattice for

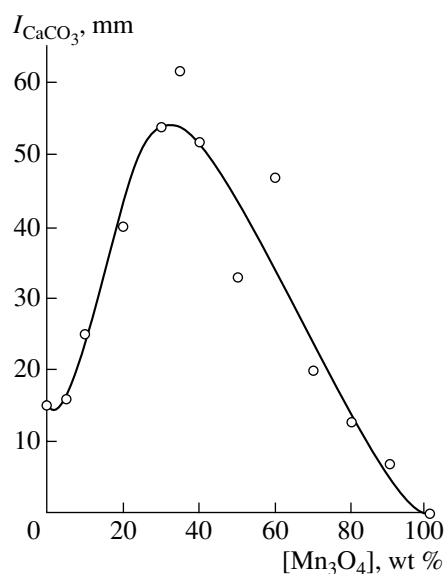


Fig. 2. The CaCO_3 concentration (the intensity of the line with $d = 3.03 \text{ \AA}$) vs. the manganese concentration in the system.

the samples with 20 and 40% Mn_3O_4 is 4.429 and 4.438 \AA , respectively. For mechanical mixtures, it is 4.444 and 4.446 \AA and coincides in fact with the tabulated value (4.445 \AA). The positions of the diffraction maxima of gibbsite formed upon talum hydration turn to be shifted relatively to the tabulated values.

A comparison of the IR spectrum of $\text{Al}(\text{OH})_3$ with that of the sample with manganese introduced (30–40% Mn_3O_4) showed that the absorption bands indicating the formation of new hydrogen bonds are present in the latter. The characteristics of the OH groups also change. The absorption band at 870 cm^{-1} characteristic of pure MnHC is absent from the spectrum of the mechanical mixture of hydrated talum and manganese hydroxycarbonate, unlike the spectrum of the sample containing 30–40% Mn_3O_4 . This points to changes in its composition.

The findings of differential thermal analysis also indicate the interaction between the components of the system. The effects corresponding to the transformations of initial manganese hydroxycarbonate (at 350 and 430°C) are absent, and instead of them, endo-effects in the 340–660°C region arise, which can be attributed to the formation of a mixed manganese–aluminum compound with the MnHC structure.

Thus, chemical interaction occurs between MnHC and calcium aluminates upon their mixing in an aqueous medium at 75°C, which, in our opinion, can be described as follows: (a) the dissolution of calcium aluminates in water to form Ca^{2+} and $[\text{Al}(\text{OH})_4]^-$ ions; (b) the hydrolysis of aluminate ions $[\text{Al}(\text{OH})_4]^- = \text{Al}(\text{OH})_3 + \text{OH}^-$; (c) the chemical interaction of MHC with the products of dissolution and the hydrolysis of

calcium aluminates. Calcium ions withdraw CO_3^{2-} ions from the structure of metal hydroxycarbonate, forming CaCO_3 ; aluminate ions replace carbonate ions in metal hydroxycarbonate and transform them into the structure close to hydrotalcite in some cases.

The equilibrium concentration of Ca^{2+} and $[\text{Al}(\text{OH})_4]^-$ ions in the solution is small but is retained constant because the removal of ions from the solution together with the reaction products is compensated by the additional transition into the solution of the same ions from high-alumina cements. Since cement hydration resulting in the nucleation of the phases of aluminum hydroxide and calcium hydroxyaluminate is rather slow, these phases can interact during nucleation, when they are highly active yet and are capable of entering to the structure of the hydroxycarbonates of supporting metals, thereby providing deep interaction between the components. The nature of interaction between MnHC and calcium aluminate in an aqueous medium is nearly the same as that in the CoHC–NiHC–calcium aluminates systems. Metal hydroxycarbonate retains the initial structure and does not transform into the structure close to that of hydrotalcite. The above findings supplemented the picture of interactions in the metal hydroxycarbonate–calcium aluminate systems and made it possible to produce various modifications of manganese catalysts for complete oxidation.

Formation of Copper–Zinc Catalysts

We continued studies aimed at the improvement of the commercial catalyst for low-temperature conversion of carbon oxide based on copper and zinc hydroxycarbonates and calcium aluminates. Because of the high concentration of copper oxide in the catalyst (up to 50%), a blend in which only a portion of the copper introduced exists as a compound with the hydrotalcite structure is formed upon the treatment of copper and zinc hydroxycarbonates and calcium aluminates with aqueous ammonia 70–75°C by the method of chemical mixing. The phases of copper and zinc hydroxycarbonates are also present, and the undesirable CuO phase is formed upon the decomposition of the copper–zinc complex that is present in the solution.

To obviate this difficulty and to achieve more uniform distribution of the copper and zinc ions over the bulk of the sample, we used a special technology in which an intermediate product (the so-called double salt) comprised of mixed copper and zinc hydroxycarbonates with the structures close to those of roasite $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$ and aurichalcite $(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$ was obtained beforehand [16, 17].

The double salt is prepared by the thermal decomposition of the copper–zinc ammonia carbonate solution with the specified Cu/Zn ratio. The precipitated salts may have a variable composition. Therefore, we attempted to find the distinctive features of diffraction patterns, which would be indicative of the structure of the

prepared salts. A distinctive sign of the structure close to roasite is the reflection (031) with $d = 2.592 \text{ \AA}$, which is absent from the diffraction pattern of copper hydroxycarbonate with the malachite structure formed under the same conditions in the absence of a zinc component. A noticeable shift of the (020) reflex provides evidence for the formation of a structure close to aurichalcite. The interplanar distance in zinc hydroxycarbonate with the hydrozincite structure is 2.17 \AA , and in the presence of a copper-containing component, the phase is formed that is characterized by the shift of the [020] reflex to the position corresponding to $d = 2.23 \text{ \AA}$. The aurichalcite/roasite ratio estimated from the ratio of the integral intensities of the lines $J_A(400)/J_P(020)$ on the diffraction pattern is an important characteristic of the product.

The technology of double salt allowed the preparation of a molded NTK-10F catalyst by heterogeneous ionic exchange in the presence of calcium aluminates using the hydrothermal treatment of molded granules. Copper hydroxycarboaluminate has the hydrotalcite structure, and the unreacted fraction remains as the double salt [18, 19]. When technology is strictly followed, the appearance of the CuO phase can be avoided.

As was mentioned above, the thermal treatment of the above compounds produces disordered oxide compounds, and reduction in the temperature range of 200–400°C leads to the separation of highly dispersed copper. A significant fraction of copper formed did not manifest itself in the diffraction patterns. A current concept on the active state of copper in the low-temperature catalysts for methanol synthesis and CO conversion suggests that active copper atoms can either be statistically distributed in the ZnO lattice or present mostly on the ZnO surface as cluster particles $<30 \text{ \AA}$ in size. Phases that form the basis of the catalyst supply these particles to the surface, retain them in an active state for a long time, and provide the mechanical strength and thermal stability of the system [3, 4, 20]. When the size of copper particles and the fraction of so called “X-ray amorphous” copper in the sample are known, one can predict the catalyst lifetime. Our *in situ* studies confirm this conclusion.

Copper-containing samples were reduced in hydrogen in a high-temperature X-ray chamber at different temperatures, and the areas of the maxima corresponding to the copper metal were determined. The fraction of “X-ray-amorphous” copper was estimated from the ratio between these areas for the samples reduced at 250 and 750°C. Copper–zinc–aluminum and copper–zinc–aluminum–calcium mechanical mixtures close in chemical compositions to the samples studied were used as reference compounds. A number of various laboratory, pilot, and commercial (domestic and imported) samples were analyzed. Statistical processing of our findings showed that the fraction of X-ray amorphous copper in inactive and unstable samples is 30–35%.

Meanwhile, in the ICI catalysts and in the best domestic catalysts, including those prepared on the basis of calcium aluminates, this fraction is higher than 70%. Note that, in the samples with a rather small fraction of X-ray amorphous copper, which rapidly sinters during the reaction or with an increase in temperature, the transformation of disordered protospinel and anion-modified solid solutions into crystallized spinels (mostly ZnAl_2O_4) and oxides also occurs. The final separation of the OH^- and CO_3^{2-} groups and supersaturated nonequilibrium solid solutions decay during thermal treatment in air or in a reductive medium at temperatures of 450–550°C.

The introduction of nonvolatile anions, which are capable of retaining in the structure at high temperatures for a long time, to hydroxycarboaluminates or hydroxycarbonates could produce stronger and more thermally stable compounds. We began the studies along these lines. Complex copper–zinc salts containing nonvolatile anions were prepared by thermal decomposition of a copper–zinc–ammonia–carbonate solution and an aqueous or ammonia solution of the additive introduced. The solution was placed into a reactor and heated to 90°C along with continuous stirring and distillation of a vapor–air mixture, which contained also ammonia and carbon dioxide. The thermal decomposition of the copper–zinc–ammonia–carbonate solution with the additives was carried out for 40–48 h. The suspension thus obtained was filtered, washed, and dried in air at 50–60°C. The samples were then calcined at ~400°C and reduced in H_2 in the regime of programmed heating to 270°C. A series of catalyst samples was prepared from anion-modified salts and calcium aluminates [21].

Anion-modified copper–zinc salts and catalysts on their basis were studied by X-ray diffraction, differential thermal analysis, thermal chromatographic, and IR-spectroscopic methods. The findings indicate that the small amounts of additives introduced into the copper–zinc system change substantially the properties of copper and zinc hydroxycarbonates. Diffraction patterns corresponding to the copper and zinc hydroxycarbonates with the structures close to those of rosasite and aurichalcite, respectively, depend on the nature of the additive. The diffraction pattern of the structure close to that of rosasite changes most noticeably, namely, the ratios of intensities change and lines broaden.

The complex salts are decomposed and reduced at 20–50°C higher temperatures than those for common double salts. The copper dispersion in the samples reduced at ~300°C increases. In the anion-modified samples after reduction, the size of copper particles is 80–90 Å, whereas 200–220 Å particles are formed upon the reduction of the common double salt. At this stage of the study, we did not find the conditions providing deep interaction of complex salts with calcium aluminates. Nevertheless, probing the catalysts in low-temperature CO conversion on a pilot setup at a pres-

sure of 2.8 MPa, a temperature of 180–370°C, and a space velocity 6000 h^{-1} for 72 h showed that they are more active than the standard NTK-10-FM sample.

The features of the formation of copper–zinc–cement catalysts (NTK-10-2F, NTK-10-2FM) were also studied. The catalysts are complex salts with the atomic distribution of copper, zinc, and aluminum, which are within strong granules obtained by the hydrothermal solidification of special cement. One of the most important advantages of a noncalcined catalyst in industry is the possibility of its safe activation without danger of overheating by gas with a high concentration of a reducing agent. Since the loading of current reactors, for example, carbon oxide converters, with catalysts reaches 70–150 tons, it is clear that feeding of excess hydrogen can result in accidental temperature jumps. The activation of a noncalcined copper–zinc–aluminum–calcium catalyst occurs in two stages: decomposition is accompanied by the endo-effect and reduction is accompanied by the exo-effect, that is, the total heat of the process is extremely small. The use of the regime developed at the Novomoskovsk Institute of Nitrogen Industry on several plants made it possible to decrease the activation time 1.5–2 times.

It became clear that under industrial conditions, the NTK-10-2F catalysts sometimes act as a wide layer. This behavior of the catalyst can be explained by the fact that reduced copper epitaxially bound to ZnO disappears from the surface due to the formation of a solid solution with ZnO, when a reductive gas is replaced for an inert gas [22]. When the sample is newly reduced, copper appears on the surface again. This is likely the reason for a decrease in the activity of the NTK-10-2F. Therefore, it is necessary to follow thoroughly the directions for preparation and activation in the converter. Then, the operation period for the catalyst will be at least 5 years, as follows from the data obtained on the Unit #2 Azot at the Novomoskovsk Nitrogen Plant.

The new modification of the NTK-10-2FM catalyst [23] (synthesized using a certain controlled ratio of compounds like aurichalcite and rosasite) loaded in an amount of 150 ton into one of the carbon monoxide converters showed a very high activity under the operating conditions. The expected catalyst service life is over five years.

Notably, the active phase in all cement-containing catalysts appears in both free and bound states. Therefore, a fraction of the active component in the aluminocalcium catalysts is reduced immediately and another portion is reduced gradually during performance or with gradual increasing the temperature, and this prolongs the catalyst lifetime. Several methanation units loaded with the NKM-4A nickel–aluminum–calcium catalysts operate up to date over 15 years [24–26].

Support or catalyst (active component)	Process (developers)	Operating temperature, °C	Mechanical strength,* MPa (specific surface area, m ² /g)	Parameters of performance
Galumin (CaO, Al ₂ O ₃)	For the catalysts for methanation, naphtha conversion, synthesis of allene, drying of gases, synthesis of aliphatic hydrocarbons, desulfurization, methanol conversion, decomposition of acetylenic alcohols, etc. (Novomoskovsk Institute of Nitrogen Industry, Institute of Organic Chemistry)	100–700	15–60 (30–350)	–
Galumin-C	"	100–750	(15–30)	–
Talum + Al ₂ O ₃	For the catalysts for high-temperature processes	100–800	(30–140)	–
NKM-4A (Ni) TU 113-03-2003-92	CO and CO ₂ methanation, O ₂ hydrogenation (Novomoskovsk Institute of Nitrogen Industry and Institute of Organic Chemistry)	180–650	C—35 ± 5 R—45 ± 5	≤10 ppm
NKM-2A (Ni) TU 113-03-00209515-64-92	CO and CO ₂ methanation, steam reforming, NH ₃ dissociation, O ₂ hydrogenation (Novomoskovsk Institute of Nitrogen Industry)	180–650 510–860 600–950 170–700	R—50–80	≤10 ppm CO, <5% CH ₄ (at 700°C)
NKM-2V (Ni) TU 113-03-00209515-64-92	CO and CO ₂ methanation, O ₂ hydrogenation (Novomoskovsk Institute of Nitrogen Industry)	175–550 170–600	R—35–60	≤5 ppm CO 5 ppm CO ₂
KDA-10A (Ni) TU 113-03-00209510-43-87	NH ₃ dissociation for obtaining protective and reductive media (Novomoskovsk Institute of Nitrogen Industry, Institute of Organic Chemistry)	650–950	R—35 ± 5 T—25–50	Residual NH ₃ ≤0.03–0.1%
KDA-11 (Ni) TU 113-03-00209510-75-95	NH ₃ dissociation (Novomoskovsk Institute of Nitrogen Industry)	650–950	R—35 ± 5 T—25–50	Residual NH ₃ ≤0.03–0.1%
KDA-1A and KDA-1M (Fe) TU 6-03-390-75 and TU 113-03-27-56-85	NH ₃ dissociation (Novomoskovsk Institute of Nitrogen Industry and State Institute of Nitrogen Industry)	650–1000	–	Residual NH ₃ ≤0.03–0.1%
NTK-10-2F and NTK-10-2FM TU 113-03-00209510-68-92	Low-temperature conversion of CO + H ₂ O (Novomoskovsk Institute of Nitrogen Industry)	200–360	F—1.5–2.0 kg per mm of the granule diameter	Residual CO concentration is 0.15–0.45%
NTK-10-2L and NTK-10-2LF TU 113-03-00209510-67-92	Low-temperature conversion of CO + H ₂ O (front layer) (Novomoskovsk Institute of Nitrogen Industry)	200–360	C—70–100 F—1.7–2.5 kg per mm of the granule diameter	Residual CO concentration is 0.18–0.5%
NTK-10-7 and NTK-10-7F TU 113-03-00209510-76-95	Refining processes (Novomoskovsk Institute of Nitrogen Industry)	100–650	F—1.5–2.0 kg per mm of the granule diameter	

Table. (Contd.)

Support or catalyst (active component)	Process	Operating temperature, °C	Mechanical strength, * MPa (specific surface area, m ² /g)	Parameters of performance
NTK-10-G (Cu, Zn)	Synthesis of 2-ethylhexanol (Novomoskovsk Institute of Nitrogen Industry and All-Russia Research Institute of Petrochemical Industry)	140–200	35 ± 5	Yield 95–99%
NTK-10-B (Cu, Zn)	Synthesis of γ -butyrolactone – dehydrogenation of 1,4-butanediol (Novomoskovsk Institute of Nitrogen Industry and All-Russia Research Institute of Petrochemical Industry in St. Petersburg)	200–300	35 ± 5	Yield 99.8%
NTK-10 (Cu, Zn) TU 113-03-00209510-44-89	Low-temperature conversion of CO + H ₂ O (Novomoskovsk Institute of Nitrogen Industry and Institute of Organic Chemistry)	200–300	C—30 ± 5 F—45 ± 5	Residual CO concentration is CO ≤ 0.15–0.5%
NTK-10-2, NTK-10-7, NTK-10-3 (Cu, Zn)	Synthesis and decomposition of methanol and water–methanol mixture, methanol conversion (Novomoskovsk Institute of Nitrogen Industry, Lomonosov State Academy of Fine Chemical Technology, Institute of Organic Chemistry)	180–400	R—55 ± 10 C—60 ± 10 F—1.5–2.5 kg per mm of the granule diameter	—
TSKA-1 (Zn)	Purification from H ₂ S (Novomoskovsk Institute of Nitrogen Industry, Institute of Organic Chemistry)	350–400	15.0–50.0	Sulfur capacity 28–30%
TSKA-2 (Zn)	Purification from H ₂ S (Novomoskovsk Institute of Nitrogen Industry, Institute of Organic Chemistry)	250–400	C—15.0–50.0	Sulfur capacity 32–32%
NKO-2-1 (Ni, Cu) TU 113-03-00209510-49-90	O ₂ hydrogenation (Novomoskovsk Institute of Nitrogen Industry, Kriogenmash, Institute of Organic Chemistry)	200–800	C—25 ± 5	Residual O ₂ concentration ≤ 5 ppm
NKO-2-2 (Ni, Cu) TU 113-03-00209510-49-90	O ₂ hydrogenation (Novomoskovsk Institute of Nitrogen Industry, Kriogenmash, Institute of Organic Chemistry)	180–700	C—30 ± 5	Residual O ₂ concentration ≤ 5 ppm
NKO-2-3 (Ni, Cu) TU 113-03-00209510-49-90	Cracking of heavy oil residues, O ₂ hydrogenation	180–750 500–600	40 ± 5.0 40 ± 5.0 F—1–1.5 kg per mm of the granule diameter	Residual O ₂ concentration ≤ 5 ppm; yield of light products 40–64%, gasoline fraction up to 57.8 ppm
NKO-2-3F	Oxidation of CH ₄ and other hydrocarbons (Novomoskovsk Institute of Nitrogen Industry and Kriogenmash)	100–750	C—30–60	Residual CH ₄ concentration ≤ 0.01 ppm
GTT	Purification of gases from ozone (Novomoskovsk Institute of Nitrogen Industry and Moscow State University)	25–110	35–40	(1–5) × 10 ⁻⁵ vol % O ₃
KTS-5 (Co, Cu)	Synthesis of aliphatic hydrocarbons from CO (Institute of Organic Chemistry, Novomoskovsk Institute of Nitrogen Industry)	210–230, reduction at 350–400	30–40	Yield of liquid hydrocarbons, 90–103 g/nm ³ , CO conversion 70–72%; selectivity to benzene fraction, 82–90%
NTK-10-1, NTK-10-3K, and NTK-2K (Cu, Zn, Ni) TU 113-03-00209510-44-89	Synthesis of butyl alcohols from aldehydes at a pressure of 280–350 atm	250–280 (180–250)	30 ± 5	Rate, 4000–5300 g (l Cat) ⁻¹ h ⁻¹ , conversion of aldehydes 98.0–99.6%

Table. (Contd.)

Support or catalyst (active component)	Process	Operating temperature, °C	Mechanical strength, * MPa (specific surface area, m ² /g)	Parameters of performance
NTK-10-3FP (NTK-10-1FKHM(M) (Cu, Zn, Ni) TU 113-03-00209510-68-92 VIG-2	Synthesis of butyl alcohols from aldehydes at pressure 280–350 atm (Novomoskovsk Institute of Nitrogen Industry, Institute of Organic Chemistry, and Salavatnefteorgsintez)	250–280 (180–250)	55 ± 10 F—1.1–1.8 kg per mm of the granule diameter	Rate, 4500–5500 g (l Cat) ^{−1} h ^{−1}
Modified NKM-2A	Glucose hydrogenolysis (VNIISintezbelok, Novomoskovsk Institute of Nitrogen Industry, and Institute of Organic Chemistry)	220 ± 10	C—25.0–35.0	5–6 cycles without regeneration, yield of glycerol and glycols 70–73%
Copper–cesium and copper–cement catalysts, galumins	Production of cyclic alcohols, synthesis of d,l-menthol at pressures 1–20 atm (Institute of Organic Catalysis and Electrochemistry, Novomoskovsk Institute of Nitrogen Industry)	110–170	C—25.0–50.0	An increase in productivity by 1.5–6 times
Vanadium–magnesium–aluminum–calcium catalyst	Synthesis of chloroorganics, production of vinyl chloride, ethylene additive oxidative chlorination, interaction of methanol with HCl (NIISintez, Novomoskovsk Institute of Nitrogen Industry, and Institute of Organic Chemistry)			Conversion and selectivity to trichloroethane at 300°C is about 100%
Modified catalysts NKO-2, NKO-2RV, and NKM	Ethylbenzene oxidative dehydrogenation to styrene (Institute of Organic Chemistry and Novomoskovsk Institute of Nitrogen Industry)		C—200–350 kg/cm ²	Selectivity 93–98%, Styrene yield >60%
Promoted copper catalysts based on galumin and galumin-TS	Thymol (2-isopropyl-5-methylphenol) hydrogenation at initial pressure 100 atm (AROMASINTEZ, Novomoskovsk Institute of Nitrogen Industry, and State Institute of Nitrogen Industry)	185–200	C—25.0–35.0	Conversion, 98.8%
NTK-10, NTK-10-7-3F, and NTK-10-7-3	Methanol dehydrogenation to methyl formate (Lomonosov State Academy of Fine Chemical Technology, Institute of Organic Chemistry, and Novomoskovsk Institute of Nitrogen Industry)	200–250		Total selectivity 65–70%, selectivity to methyl formate 80–85%
NTK-10-7FP, NTK-10-7-3F, and NTK-10-7-5, TU 113-03-00209510-76-95	Synthesis of aniline by nitrobenzene hydrogenation (All-Russia Research Institute of Petrochemical Industry, NPO OKSOKhimneft', and Novomoskovsk Institute of Nitrogen Industry)	180–280	F—1.5–2.2 kg per mm of the granule diameter	Yield of aniline >99%, selectivity 99.0–99.5%
Modified catalyst NTK-10-7	Cyclohexanol dehydrogenation (Novomoskovsk Institute of Nitrogen Industry and State Institute of Nitrogen Industry)	240–260	C—250–500 kg/cm ² F—1.5–2.0 kg per mm of the granule diameter	Conversion 65–70%, selectivity 98–99%
	Dehydrogenation of ethanol to ethyl acetate (Institute of Organic Synthesis and Novomoskovsk Institute of Nitrogen Industry)	200–250	"	Ethanol conversion 50%, selectivity 80%
Modified catalysts NTK-10 etc.	Synthesis of dimethyl ether (Novomoskovsk Institute of Nitrogen Industry, and Institute of Petrochemical Synthesis)	220–280	"	At CO conversion of 40–70%, conversion to DME is 50–80%, at CO conversion of 20–30%, conversion to DME is 70–90%

* C—cylinders, R—rings, T—pellets, and F—formed catalyst.

Mechanochemical Synthesis of Catalysts

In the last few years, the methods of mechanical activation of raw materials were developed and scientific bases for mechanochemical synthesis of catalysts were created [27].

The treatment of the catalyst with high-pressure water jets (up to 300 MPa and sometimes even higher) is, in our opinion, a promising method for mechanical activation. Such a treatment affects the activity and other physicochemical characteristics of catalysts. To study major factors affecting the parameters of technological processes based on the use of the energy of high-pressure jets, a special setup was developed at the Tula State University [28, 29]. Water under a high pressure is fed to a hydroinstrument and then passes through a jet-forming attachment to a mixing chamber. Due to vacuum created by a water jet, a ground catalyst is simultaneously injected from a loading device into a jet and saturates water in the mixing chamber. A mixture formed falls into a collimator where the suspension jet is finally formed. A jet after impact to the surface of a support is caught, and the catalyst is separated. The material obtained is ground with high-speed rotating milling balls of cylinders. A continuous process is achieved by the removal of the target fraction from the reactor and feeding the raw material and high-pressure water.

X-ray diffraction studies of the profile of the diffraction reflections, their positions, and integral intensities show that the action of high-pressure water is different depending on the chemical nature, structure, and other characteristics of substances treated. In some cases, for example, during treatment of α - Al_2O_3 or ZnO , the broadening of diffraction lines is found, which can be due to grinding the crystals and the appearance of microdistortions. The shift of lines, a decrease in their intensity, and arising asymmetry found on the diffraction patterns of copper and zinc hydroxycarbonates indicate the presence of various defects.

A nickel-copper-aluminum precursor of the NKO-2 cement-containing catalyst for refining industrial gases was treated with high-pressure water jets. A mechanical mixture of copper, nickel, and active alumina was treated in the reactor for 2–3 min. The catalyst obtained after filtration and drying in air was investigated by various physicochemical methods. A simple mechanical mixture of the same components was studied in parallel for comparison. Even short-term treatment was found to produce the partial amorphization of the sample and to facilitate the interaction between the components and mainly the formation of a copper-nickel solid solution, which is well known to provide high refining activity after reduction. Work is underway to modify the reactor in order to increase the time and efficiency of treatment.

Preparation of Cement-Containing Catalysts by Impregnation

A significant part of studies performed previously dealt with the synthesis of catalysts by chemical mixing. Recently we began a study of the formation of the supported cement-containing catalysts.

The aluminum-calcium support for the NIAP-18 catalyst for natural gas steam conversion and the support for NIAP-22 also applied in this process were used to prepare impregnated samples. The main phases of the support for NIAP-18 are α - Al_2O_3 and $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (denoted as CA_6). The support is produced in the form of rings with the dimensions 15×10^7 mm. The main phase of the support for NIAP-22 produced in a cylinder shape with seven holes is α -alumina. Impregnation was carried out with aqueous solutions of Ni, Cu, Mn, and Al nitrates [30]. The concentration of the active components was 15 wt %. X-ray diffraction analysis showed that the modified copper and nickel oxides are formed in the samples upon impregnation, drying, and calcination at 400°C and a fraction of the nickel-containing phase interacts with manganese compounds to form NiMnO_3 . After reduction with hydrogen, the nickel crystal lattice parameter changes because of the incorporation of copper and the deformation of the nickel-copper alloy. The lattice parameter of this alloy depends on the NiO/CuO ratio in the sample. At NiO/CuO ≈ 3.2 , the parameter $a_0(\text{Ni-Cu})$ is 3.552 Å and, at NiO/CuO ≈ 0.25 , $a_0(\text{Ni-Cu})$ is 3.577 Å. The copper crystal lattice is less distorted, and $a_0(\text{Cu}) = 3.621$ Å, while the tabulated value is 3.615 Å.

In the range of compositions of NiO, 9.5–10.5%, CuO, 3.5–4.0%, and MnO_2 , 0.5–0.8%, the samples are most active in the reduction of nitrogen oxides with methane and in carbon monoxide oxidation.

According the X-ray diffraction data, all catalysts prepared using the above supports of an optimal composition are identical and include α - Al_2O_3 , CA_6 , and NiO. The CuO phase was not found, and the NiO dispersion in all samples was 85–125 Å.

Reduction occurs in three stages. At the first stage (220–230°C), CuO is reduced and at the second (300–310°C) and third (420–430°C) stages, free NiO and NiO bound with the support are reduced. As a result of reduction, the parameter of the Ni crystal lattice changes because of copper incorporation and a Ni-Cu alloy with the dispersion of 170–190 Å is formed. A mechanical strength of the catalyst is comparable with that of the initial supports.

Commercial Cement-Containing Catalysts from the Novomoskovsk Institute of Nitrogen Industry

It is well known that in chemical industry, petrochemistry, metallurgy, machinery, and other branches of the Russian industry, 200–250 catalysts are used and renewed each 5–6 years [31–33]. The Novomoskovsk Institute of Nitrogen Industry has specialized for more

than 40 years in developing and producing the catalysts [25, 26], and several tens of them operate efficiently on ~200 plants in Russia, CIS, and abroad.

The catalysts based on special purity high-alumina cements, which were developed together with other institutions, fill a distinct place among the catalysts created. They are used for low-temperature and high-temperature methanation, low-temperature carbon oxide conversion, the creation of protecting atmospheres, the synthesis of butyl alcohols, 2-ethylhexanol, γ -butyrolactone, acrylamide, aniline, methyl formate, dimethyl ether, methane conversion, the manufacture of synthetic gasoline, ethyl acetate, glycerol, cyclohexanol dehydrogenation, the synthesis and conversion of methanol, heavy residue cracking, ammonia oxidation, the synthesis of d,l-menthol, the manufacture of ethylbenzene, styrene, and allene, the synthesis of chlorine-containing substances, etc. [6, 7, 24–26]. The cement-containing catalysts have high activity, mechanical strength, thermal stability, selectivity, long lifetime, and resistance to coking. The elucidation of the physicochemical bases for the synthesis of oxide and metal oxide cement-containing catalysts favored the development of low-waste technology for their preparation on the industrial equipment of the Novomoskovsk Institute of Nitrogen Industry the Dorogobuzh plant catalyst manufactures [25, 26].

In the last few years, a series of noble-metal-free catalysts for the refinement of industrial and exhaust gases were developed at the Novomoskovsk Institute of Nitrogen Industry together with other research institutions and plants. The following cement-containing compositions were used: copper, nickel, nickel–copper, nickel–copper–manganese, manganese, copper–zinc, copper–nickel–zinc, copper–nickel–manganese, cobalt, cobalt–copper, cobalt–copper–magnesium, magnesium, copper–magnesium, zirconium, and others. It is well known that many units the refining of gases operate under atmospheric pressure. Therefore, an important advantage of these catalysts is the possibility of their production not only in the form of pellets or balls but also as rings and blocks. These catalysts are at least 8–45 times cheaper than widely used platinum and palladium catalysts.

New cement-containing catalysts and adsorbents for the refining of exhaust gases of industrial plants for the production of isoprene, phenol, acetone, chlorinated organic products, for refining transformer oils, etc., are tested now. The possibility of charging the neutralizers for the refining of exhaust gases of diesel engines with the modified catalysts of the NKO-2, NTK-10-7, etc., series as well as their use the refining of the exhaust gases of the processes of methanol, dimethyl ether, and methyl formate decomposition are elucidated. The catalysts for methanol synthesis are also tested [34–38]. The modernization of base catalysts is continued, and the technology for producing granules with small diameters (3.5 and 2.8 mm) and controlled length is devel-

oping. The characteristics of the above catalysts in various technological processes are investigated.

The catalyst manufacture of the Novomoskovsk Institute of Nitrogen Industry produces catalysts and supports in the scale from tens of kilograms to hundreds of tons (see the table). More than 2000 tons of cement-containing catalysts for many processes of organic, inorganic, and environmental catalysis have been made and sent to industry. The regimes of charging, reduction, passivation, and performance were developed for all catalysts.

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