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Thermolysis of Coprecipitated Copper(II)–Nickel(II) Hydroxides

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Abstract—Coprecipitated copper(II)–nickel(II) hydroxides and mechanical mixtures of these were obtained at varied metal ion ratio and time of mother liquor aging and studied by potentiometric titration, chemical and differential thermal analyses, IR spectroscopy, and X-ray phase analysis.

Hydroxide–oxide compounds are widely used as materials in various fields of science and technology, in particular, as rather inexpensive and stable catalysts [1]. For example, it has been shown that systems containing aqua and hydroxo complexes of copper(II) and nickel(II) are promising catalysts for selective oxidation of alkanes [2–5]. It is also known that some industrial processes of basic organic and petrochemical syntheses are performed with copper- and nickel-containing catalysts, including those of the oxide–hydroxide type [6–8]. Catalysts of this kind are mainly obtained by mixing of the appropriate oxides followed by thermal treatment [9, 10]. However, this method fails to always yield complex materials with sufficient reproducibility. Moreover, the ceramic synthesis technology employs high temperatures, which leads to energy losses and frequently impairs the catalytic activity of the synthesized materials. Therefore, coprecipitation of hydroxides is in some cases a more promising route to mixed copper–nickel systems containing hydroxo and oxo groups [9].

The results of previous studies established the formation of unstable heteronuclear hydroxo complexes of copper–nickel in aqueous solutions [11, 12]. It has been proposed to rely upon this fact in developing a new synthesis method based on formation in solution of unstable hydroxo complexes involving metal ions, passing subsequently into a solid phase which acts as a precursor for the target materials [13].

Apparently, to implement this idea, it is necessary to study in detail the conditions under which hydroxide precipitates can be obtained, the processes of their thermal decomposition, and products formed in these processes by various analytical methods, and just this was the purpose of the present study.

Potentiometric titration was performed with temperature control (±0.1°C) on a pH-150 pH-meter-millivoltmeter. Glass electrode of the ESL-15-11 type and silver chloride electrode of the EVL-1M4 type served as measuring and reference electrodes, respectively; the pH measurement error was ±0.02 pH units. The titration was done as follows: 1 M NaOH solution was added from a burette with scale division value of 0.02 ml to the starting mixture of 1 M Cu(II) and Ni(II) nitrates. To obtained comparable results and simplify the interpretation of the titration curves, the added NaOH volume was converted to the molar ratio $[OH^-]/[M^{2+}]$.

With account of the potentiometric titration data, solid phases were isolated by gradually adding to the starting mixture of 1 M Cu(II) and Ni(II) nitrates, with continuous stirring, 1 M NaOH solution in a stoichiometric ratio of 1 : 2, respectively. The obtained solid phases were homogenized for 5 min and filtered off under a vacuum, washed 3 or 4 times with water and then $i\text{-}C_3H_7OH$ to negative reaction for NO_3^- ions [14], dried at 30–40°C in an oven, and analyzed. For comparison purposes, mechanical mixtures of Cu(II) and Ni(II) hydroxides (MMHs) were obtained under identical conditions at the same Cu(II) : Ni(II) ratios and studied in a similar way. To reveal the effect of the time of aging of the hydroxide precipitates on their properties, samples were also synthesized at Cu : Ni ratio of 1 : 1 and aging time of 24 and 72 h.

In making chemical analysis, a weighed portion of a hydroxide was dissolved in concentrated HNO_3 and analyzed. The total content of copper(II) and nickel(II) was found complexometrically with murexide; that of nickel(II), by direct titration with Na_2EDTA in ammonia buffer with murexide after masking Cu^{2+} with thiosulfate ions [15, 16]; and that of copper(II), as the difference of the first two quantities. Differential thermal analysis was done on an MOM derivatograph (Hungary) at a heating rate of 10 deg $\min^{-1}$ and sensitivity of DTA and DTG galvanometers of 1/10; 0.500-g samples were heated from room temperature to 1000°C, with calcined aluminum oxide used as reference. The IR spectra (KBr pellets) were taken on a Specord 75-IR spectrophotometer in the range 4000–400 cm^{-1}. X-ray diffraction patterns of the samples were taken on a DRON-3 diffractometer with CuK_α radiation and Ni filter at a scanning rate of 2 deg $\min^{-1}$.

Figure 1 shows the curves of titration with NaOH solution of aqueous Cu(II), Ni(II), and Cu(II)–Ni(II) nitrate solutions with varied ratio of metal ions. The titration curve of a nitrate solution of copper(II) shows two equivalence points (curve *1*). The jump in the pH range 4.3–4.9 at $[OH^-]/[M^{2+}]$ = 1.5–1.8, with the equivalence point at pH 7.0, $[OH^-]/[M^{2+}]$ = 1.7, corresponds to complete precipitation of polynuclear hydroxo complexes of copper(II) [17]. Addition of alkali to the system at pH 9.45 and $[OH^-]/[M^{2+}]$ = 1.8–2.3 does not lead to any increase in pH and corresponds to conversion of polynuclear hydroxo complexes into mononuclear hydroxides. On further introduction of OH groups into the system, the hydroxide suffers no changes, and the steep increase in pH (second jump) is presumably associated with coordination saturation of metal ions with hydroxide ligands and appearance of an excess of free OH groups in solution. In potentiometric titration of nickel nitrate (curve *2*) in the pH range 6.1–7.6 at $[OH^-]/[M^{2+}]$ = 0.0–1.5, mononuclear hydroxides are formed with minor precipitation. Intense precipitation of Ni(II) ions coincides with the onset of the jump at pH 7.6, with the equivalence point (pH 9.6, $[OH^-]/[M^{2+}] \cong$ 2.0) corresponding to complete precipitation of nickel(II) in the form of polynuclear compounds [12, 15].

The titration curves of a mixture of Cu(II) and Ni(II) nitrate solutions (Fig. 1, curves *3*–*5*) show three jumps. The first of these corresponds to precipitation of polynuclear copper(II) compounds, which is confirmed by the close pH values of the equivalence points of binary solutions and a Cu(II) nitrate solution. The second jump corresponds to precipitation of polynuclear nickel(II) compounds, and the third, presumably, to precipitation of a heteronuclear hydroxide. It can be seen that despite the similarity of the titration curves for individual and binary systems, the latter cannot be considered additive. This fact also confirms the possibility of formation, together with two fractions of homopolymers, of a certain amount of a heteropolynuclear hydroxide precipitate [11, 12].

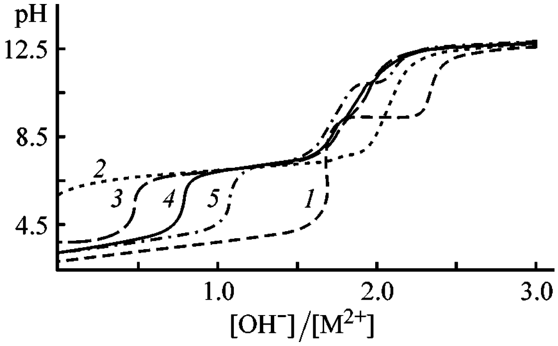

Fig. 1. Potentiometric titration curves of aqueous solutions of nitrates of (*1*) copper(II), (*2*) nickel(II), and (*3*–*5*) mixtures of these with varied content of Cu(II). Content of copper(II) (wt %): (*3*) 30, (*4*) 50, and (*5*) 70.

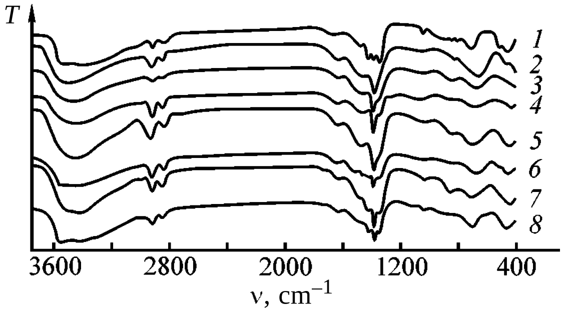

Fig. 2. IR spectra of hydroxides. (*T*) Transmission and (ν) wave number. Hydroxide (wt %): (*1*) 100 Cu; (*2*) 100 Ni; (*3, 4*) 30 Cu, 70 Ni; (*5, 6*) 50 Cu, 50 Ni; and (*7, 8*) 70 Cu, 30 Ni. (*3, 4, 5*) CPH and (*4, 6, 8*) MMH.

The results of IR spectral studies of coprecipitated hydroxides (CPHs) and MMHs (Fig. 2) indicate the presence in them of various kinds of water. The presence of a broad band of stretching vibrations of H_2O at 3650–3100 cm^{-1} points to stronger hydrogen bonds between OH^- groups. These bands are more intense and shifted to longer wavelengths in the case of CPHs (spectra *3, 5, 7*), which indicates an additional stability of CPHs ensured by the formation of intramolecular hydrogen bonds between aqua and hydroxo ligands [18]. Bending (1630–1625 cm^{-1}) and rocking (845–830 cm^{-1}) vibrations of H_2O indicate the presence of coordination-bound water in the compound. As shown by the IR spectra of nickel(II) and copper(II) hydroxides (Fig. 2, spectra *1, 2*), and also by published data [19, 20], the bands peaked at 1387–1350 cm^{-1} can be attributed to bending vibrations of OH groups bonded to copper(II) and nickel(II) atoms. The absorption peaks at 1060–1035 and 700–500 cm^{-1} may belong to bending vibrations of the bridging M–O–M bonds (M = Cu or Ni), and the bands at 400–500 cm^{-1} cor-

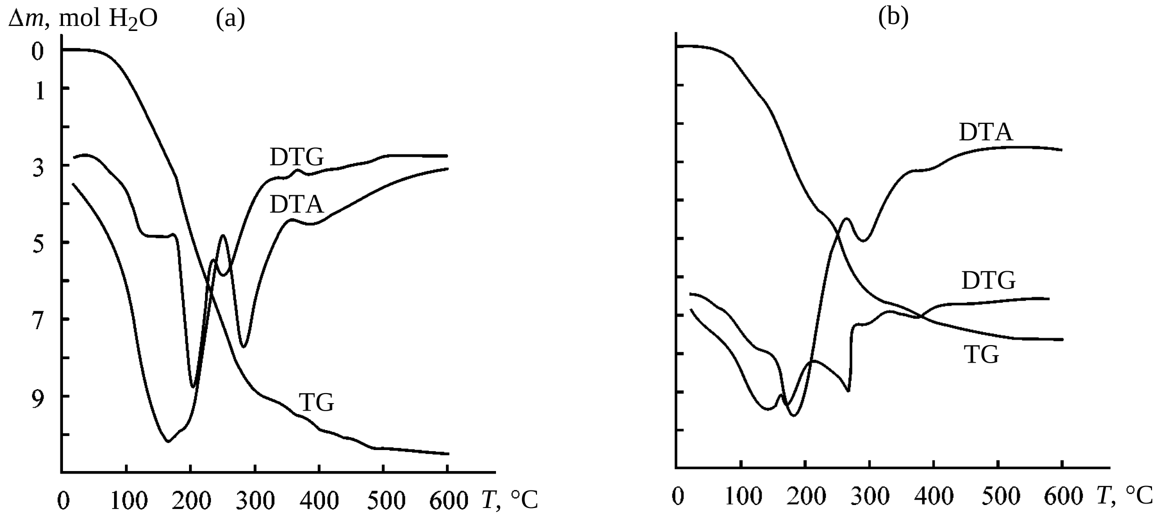

Fig. 3. Thermogravigrams of (a) CPH and (b) MMH of composition 30% Cu(II) + 70% Ni(II). (Δ*m*) Weight loss and (*T*) temperature.

respond to stretching vibrations of M–O bonds. It should be noted that the IR spectra of MMHs are more complex than those of CPHs because of the splitting of the ν(H–OH) and δ(H–OH) bands into doublets and triplets (spectra *4, 6, 8*). In addition, in CPHs with the Cu(II) content[1] of 30 and 50% (spectra *3, 5*), bands of some characteristic vibrations are shifted by 10–30 cm^{-1} to smaller wave numbers, which may be due to formation of heteronuclear structures in the hydroxide precipitate [12].

Table 1. XPA data for products formed in decomposition of hydroxides of composition 30% Cu(II) + 70% Ni(II) at 1000°C

d_{exp}	I/I_0, %	d_{ref}	*hkl*	Phase
Coprecipitated hydroxides				
2.426	100	2.426	101, 031	Ni_2CuO_3
2.181	3	2.168	002	"
2.098	68	2.093	200	$Cu_{0.2}Ni_{0.8}O$
1.482	42	1.479	220	"
1.453	3	1.463	200, 060	Ni_2CuO_3
1.284	2	1.296	103	"
1.262	11	1.262	311	$Cu_{0.2}Ni_{0.8}O$
1.198	17	1.212	202, 062	Ni_2CuO_3
Mechanical mixture of hydroxides				
2.755	2	2.751	110	CuO
2.531	9	2.530	002	"
2.422	87	2.416	111	$Cu_{0.2}Ni_{0.8}O$
2.332	9	2.323	111	CuO
2.099	100	2.093	200	$Cu_{0.2}Ni_{0.8}O$
1.855	3	1.866	202	CuO
1.483	54	1.479	220	$Cu_{0.2}Ni_{0.8}O$
1.400	2	1.410	311	CuO
1.379	2	1.375	220	"
1.315	1	1.304	311	"
1.262	18	1.262	311	$Cu_{0.2}Ni_{0.8}O$
1.209	16	1.208	222	"

To confirm this assumption and determine the content of water, the obtained CPH and MMH were subjected to thermal analysis. The weight loss curve (Fig. 3) was recalculated to moles of H_2O, which furnishes an opportunity to directly analyze the obtained thermogravigrams of decomposition of the hydroxide precipitate in terms of stoichiometry. The DTA curve of CPH of the composition 30% Cu(II) + 70% Ni(II) (Fig. 3a) shows three endothermic peaks in the intervals 40–240, 240–360, and 360–480°C. The first endothermic effect corresponds to deaquation with the loss of 7.23 mol of crystallization water, and the second and third, to liberation of 3.33 mol of bound water, equivalent to loss of 6.66 mol of OH^- groups, with a mixed oxide formed. An X-ray phase analysis of this oxide (Table 1) demonstrated the presence of approximately equal amounts of two complex oxide phases: Ni_2CuO_3 (orthorhombic crystal system, a = 2.925, b = 8.775, c = 4.336 Å) and $Cu_{0.2}Ni_{0.8}O$ (cubic crystal system, a = 4.217 Å).

A chemical analysis of the obtained hydroxides, both freshly precipitated and aged for 1 and 3 days (Table 2), demonstrated that the molar ratios of Cu(II) and Ni(II) ions in the starting solutions and the hydroxides coincide, which points to complete precipita-

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[1] Here and hereinafter, molar percents.

Table 2. Data of thermogravimetric and chemical analyses of copper(II)–nickel(II) hydroxides

Composition, %	Temperature of endothermic effect, °C				Weight loss, wt %					CuO : NiO : H_2O molar ratio
	I	II	III	IV	I	II	III	IV	Σ	
30 Cu(II)–70 Ni(II):										
CPH	40–240 (165)*		240–360 (280)	360–480 (380)	27.0 (6.66)**		11.4 (2.81)	3.6 (0.89)	42.8	1 : 2.33 : 10.56
MMH	40–160 (140)	160–260 (180)	260–360 (285)	360–510	10.0 (2.18)	14.6 (3.17)	6.8 (1.48)	3.3 (0.74)	35.2	1 : 2.33 : 7.66
50 Cu(II)–50 Ni(II):										
CPH	40–190 (130)	190–250	250–350 (280)	350–520	12.0 (1.53)	9.5 (1.22)	8.29 (1.05)	3.8 (0.45)	33.0	1 : 1 : 4.25
MMH	40–140	140–250 (170)	250–340 (280)	340–520	7.0 (0.90)	14.8 (2.25)	7.8 (0.66)	3.0 (0.38)	32.8	1 : 1 : 4.23
50 Cu(II)–50 Ni(II), 1 day:										
CPH	40–160 (140)	160–220 (180)	220–330 (265)	330–500	11.0 (1.42)	9.2 (1.18)	10.1 (1.3)	2.7 (0.35)	33.4	1 : 1 : 4.3
MMH	40–160	160–250 (175)	250–350 (290)	350–500 (385)	10.0 (1.30)	12.0 (1.56)	6.7 (0.87)	3.3 (0.43)	32.0	1 : 1 : 4.16
50 Cu(II)–50 Ni(II), 3 days:										
CPH	40–240 (140)		240–400 (290)	400–500	18.0 (2.37)		15.2 (2.09)	1.8 (0.24)	35.0	1 : 1 : 4.61
70 Cu(II)–30 Ni(II):										
CPH	40–155	155–235 (180)	235–380 (260)	380–500	8.1 (1.72)	12.6 (2.77)	9.3 (1.87)	1.8 (0.38)	31.8	2.33 : 1 : 6.74
MMH	40–140 (110)	140–240 (155)	240–330 (260)	330–520	8.0 (1.69)	16.2 (3.41)	4.4 (0.93)	2.8 (0.59)	31.4	2.33 : 1 : 6.62
100 Cu(II)	40–140	140–320 (160)		320–460	6.0 (0.37)	20.8 (1.28)		7.6 (0.47)	28.4	1 : 0 : 1.75
100 Ni(II)	40–240		240–360 (275)	360–500 (385)	24.8 (1.72)		11.2 (0.75)	4.0 (0.3)	40.0	0 : 1 : 2.77

* Peak temperature.

** Mole of H_2O.

tion of metal ions with the initial component ratio preserved in the precipitate. In this case, the following scheme of dehydration of the obtained CPH composed of 30% Cu(II) + 70% Ni(II) can be proposed:

$$\mathrm{CuNi_{2.33}(OH)_{6.66}\cdot 7.23H_2O} \xrightarrow[-7.23\mathrm{H_2O}]{} \mathrm{CuNi_{2.33}(OH)_{6.66}}$$

$$\xrightarrow[-3.33\mathrm{H_2O}]{} \sim 0.8(\mathrm{Ni_2CuO_3} + \mathrm{Cu_{0.2}Ni_{0.8}O}).$$

Thermal decomposition of MMH composed of 30% Cu(II) + 70% Ni(II) (Fig. 3b) occurs in a different way. The splitting of the endothermic peak at 40–260°C in two: at 40–160°C with a peak at 140°C and at 160–260°C with a peak at 180°C, points to a more complicated nature of deaquation of a mixture of copper(II) and nickel(II) hydroxides. No similarity in amounts of removed water is observed between CPH and MMH, although the endothermic effects occur in virtually the same temperature intervals (Fig. 3). Moreover, the total loss of water is 7.66 mol, which is 2.9 mol less than in the case of CPH of the same composition. Thus, the hydroxides, the processes of their thermal decomposition, and the resulting products exhibit specific features depending on the preparation procedure (coprecipitation or mechanical mixing). An X-ray phase analysis of the products of decomposition of MMH containing 30% Cu(II) and 70% Ni(II) (Table 2) demonstrated the presence of a $\mathrm{Cu_{0.2}Ni_{0.8}O}$ phase with minor CuO admixtures (up to 10%), with the $\mathrm{Cu_{0.2}Ni_{0.8}O}$ phase probably formed via sintering of CuO and NiO oxides.

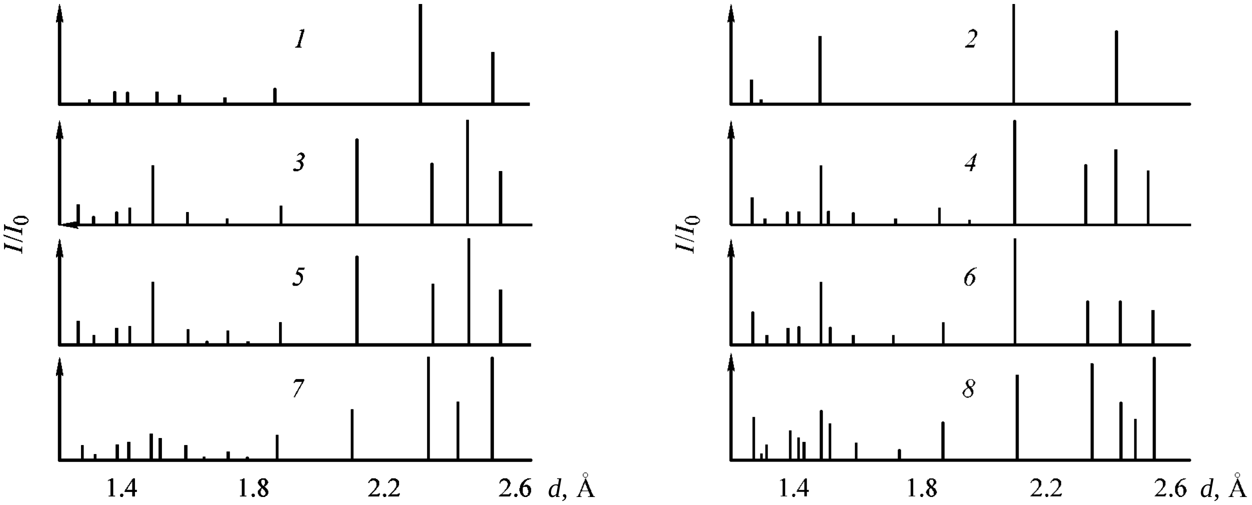

Fig. 4. X-ray diffraction patterns of the products of decomposition (T = 1000°C) of (*1*) copper(II) and (*2*) nickel(II) hydroxides, (*3, 5–7*) copper(II)–nickel(II) CPHs, and (*4, 8*) MMHs. (I/I_0) Relative intensity and (d) interplanar spacing. Initial content of copper(II) (wt %): (*3–6*) 50 and (*7, 8*) 70; aging time (days): (*5*) 1 and (*6*) 3.

Thermogravimetric analysis of CPH and MMH containing 50% Cu(II) and 50% Ni(II) also revealed differences in their dehydration. Despite the close temperature intervals of the main endothermic effects, they differ in the amount of removed water. The total amount of water in CPH somewhat exceeds that in the corresponding MMH, increasing on passing from an unaged sample to a hydroxide isolated after 3 days of aging under mother liquor. This may be due to decomposition, in the course of precipitate aging, of a part of heteronuclear copper(II)–nickel(II) hydroxide, accompanied by disintegration of hydroxo bridges and subsequent aquation of metal ions. Thus, the longer the time of CPH aging, the smaller the amount of heteronuclear hydroxide it contains. An additional argument in favor is the amount of double oxide indicated by X-ray diffraction patterns of the products of complete decomposition (T = 1000°C) of mixed hydroxides (Fig. 4). The products of decomposition of CPH containing 50% Cu(II) and 50% Ni(II) (patterns *3, 5, 6*) contain phases of CuO (interplanar spacings 2.530, 2.323, 1.886, and 1.418 Å), NiO (2.088, 1.476, 1.259 Å), and $NiCuO_2$ (tetragonal crystal system, a = 4.121, c = 4.355 Å) with the main reflections at 2.427, 1.500, 1.302, 1.251, and 1.213 Å. With increasing time of aging of the initial CPH, the intensities of CuO and NiO reflections grow and the signals from $NiCuO_2$ become weaker (2.427, 1.213 Å); the reflections at 1.500, 1.302, and 1.251 Å totally disappear from the X-ray diffraction patterns of the decomposition products of CPH, subjected to aging for 1 and 3 days (Fig. 4, patterns *5, 6*). A correlation is observed between the increasing time of CPH aging and the decreasing intensity of signals from $NiCuO_2$ in the products of its decomposition. For example, an X-ray diffraction pattern of a product of CPH decomposition (3 days of aging) shows only a single $NiCuO_2$ band (2.427 Å) with intensity of 49% (pattern *6*). It should be noted that the X-ray diffraction patterns of decomposition products of MMH containing 50% Cu(II) and 50% Ni(II) show no double oxide phase, with only the CuO and NiO phases present, which also confirms the occurrence of a chemical interaction between Cu and Ni atoms in CPH formation, just in the stage of coprecipitation, rather than in that of thermal treatment.

An X-ray phase analysis of decomposition products of CPH and MMH containing 30% Cu(II) and 70% Ni(II) (Fig. 4, patterns *7, 8*) demonstrated the presence of only copper(II) and nickel(II) oxide phases. However, the thermal behavior of the given CPH and MMH is not additive with respect to the temperature intervals of endothermic effects and weight loss (Table 1), and the total weight loss is practically the same (31.8 and 31.4%, respectively). This can be accounted for by the different physical properties (density, porosity, specific surface area) of the hydroxides obtained by coprecipitation and mechanical mixing [21].

Thus, a technique is proposed on the basis of the investigation performed for obtaining copper(II)–nickel(II) CPH whose thermal treatment can yield new inorganic materials and, in particular, catalytic systems applicable in organic and petrochemical syntheses. The temperature intervals in which various kinds of water are removed were determined and differences were revealed between the thermal properties of CPH and MMH whose dehydration occurs under milder conditions because of the absence of Cu–OH–Ni bridge bonds and is accompanied by liberation of a lesser amount of water. The phase composition of the products of CPH and MMH decomposition at $T = 1000°C$ was determined; it was shown that complex oxide compounds Ni_2CuO_3, $Cu_{0.2}Ni_{0.8}O$, and $NiCuO_2$ are present together with the CuO and NiO phases. The optimal hydroxide composition [30% Cu(II) + Ni(II)] was determined at which the yield of double oxides reaches 100% (Table 1), and the efficiency of preparing these compounds from unaged CPH was confirmed.

CONCLUSIONS

(1) A procedure was developed for synthesizing coprecipitated copper(II) and nickel(II) hydroxides, ensuring formation of complex oxide catalysts with molecular distribution of the components.

(2) The optimal composition [30% Cu(II) + 70% Ni(II)] of hydroxide whose thermal decomposition gives double oxides in up to 100% yields was determined.

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