

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Copper-Containing Catalysts for the Oxidative Dehydrogenation of Organic Compounds

O. N. Krasnobaeva^a, I. P. Belomestnykh^b, T. A. Nosova^a, T. A. Elizarova^a,
G. V. Isagulyants^b, and V. P. Danilov^a

^a Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia

^b Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia
e-mail: danilov@igic.ras.ru

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Abstract—A method of doping magnesium aluminum hydrotalcites, which are precursors for oxidative dehydrogenation oxide catalysts of various compositions, with copper(II) was developed, and copper(II)-containing oxide catalyst samples were synthesized. The catalytic properties of these catalysts were studied in the oxidative dehydrogenation of ethane, propane, and hexane. The conversion of ethane into ethylene on the copper-containing catalysts was established to proceed with high selectivities (90–97%) and at low temperatures (400–450°C).

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This work continues studies of the effect of the composition of hydrotalcite-like hydroxosalts used as catalyst precursors on the catalytic properties of the resulting catalysts for oxide catalysts of oxidative dehydrogenation of organic compounds.

In our earlier works [1–8], we synthesized different (Mg-Al, Mg-Ni-Al, Mg-Ni-Co-Al, Mg-Al-Cr, and Mg-Al-Fe) hydroxosalts containing nitrate, carbonate, decavanadate, paramolybdate, metatungstate, hexaniobate, and pentatantalate ions in their anionic interlayers. The oxide catalysts prepared from them were highly selective and provided high yields of target products in the oxidative dehydrogenation of some organic compounds.

The objective of our work was to develop a method of doping the catalysts with copper(II) and to study its effect on the properties in these catalysts the oxidative dehydrogenation of alkanes.

EXPERIMENTAL

Precursors were synthesized via the reaction of a solution of magnesium, aluminum, and copper(II) nitrates with a solution of potassium hydroxide and potassium carbonate and subsequent anion exchange of nitrate and carbonate ions for different polyoxometalate ions, in the following way.

To a solution of aluminum (0.3 mol/L), magnesium (0.6 mol/L), and copper (0.005–0.04 mol/L) nitrates, a solution of potassium hydroxide and potassium carbonate (2 mol/L KOH + 1 mol/L K₂CO₃) was slowly added drop by drop (1 drop per 3 s) under continuous stirring at 60°C until pH changed from 1 to 10.

The resulting precipitate was washed with water from potassium ions on a Nutsche filter until the washings gave negative reaction to tetraphenylborate. According to chemical and X-ray diffraction analyses, the precipitate represented a ternary magnesium copper aluminum hydrotalcite-like hydroxosalt [AlMg₂Cu_{0.125–0.02}(OH)_{5.25–5.04}][(CO₃)_{0.5} · nH₂O], isomorphous to various binary and ternary hydrotalcite-like hydroxosalts synthesized by us earlier [1–5]. To accomplish anion exchange with a partial substitution of decavanadate (V₁₀O₂₈)^{6–}, paramolybdate (Mo₇O₂₄)^{6–}, and metatungstate (H₂W₁₂O₄₀)^{6–} ions for the carbonate ions of a hydroxosalt, the paste obtained after precipitation and washing was diluted with water to the ratio solid (S) : liquid (L) = 1 : 2; then, a solution of potassium decavanadate (0.15 mol/L), ammonium paramolybdate (0.15 mol/L), or sodium tungstate (0.5 mol/L) was added in a necessary amount depending on the required final composition. The pulp was stirred for 10 min, then nitric acid (0.2 M) was added to it drop by drop until pH became 4.5 in order to exchange the carbonate ion for the decavanadate or paramolybdate ions [9, 10] and until pH became 5.0 in order to exchange the carbonate ion for the metatungstate ion [11]. After keeping the mixture at required pH for 10 min to exchange the carbonate ion for the decavanadate and paramolybdate ions and for 30 min to exchange the carbonate ion for the metatungstate ion, the precipitate was filtered off and washed with water from potassium, ammonium, and sodium ions.

To perform the anion exchange of the carbonate ion of the Mg-Cu-Al hydroxosalt for the polyoxoniobate [Nb₆O₁₉]^{8–} and polyoxotantalate [Ta₅O₁₆]^{7–} ions,

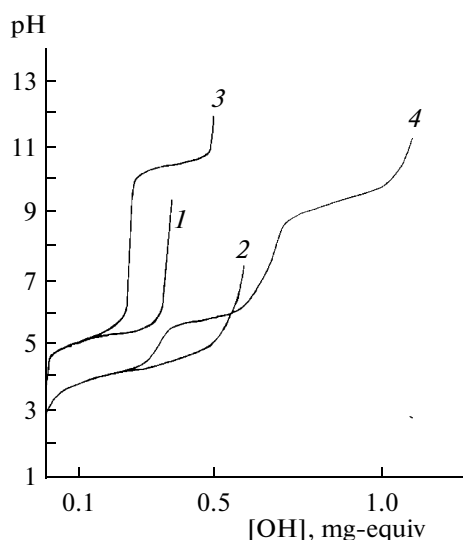


Fig. 1. Potentiometric titration curves for solutions of (1) copper nitrate, (2) aluminum nitrate, (3) copper and magnesium nitrates, and (4) copper, aluminum, and magnesium nitrates.

we used the solution obtained by dissolving the products of alloying K_2CO_3 with Nb_2O_5 at a molar ratio of 10 : 1 (pH 13) and the product of alloying K_2CO_3 with Ta_2O_5 at a molar ratio of 50 : 1 (pH 13), respectively. Anion exchange lasted 6 h, after which the precipitate was washed with water from potassium ions [12].

The phase and chemical compositions of the synthesized hydroxosalts were determined using chemical analysis, X-ray diffraction (DRON-2.0 diffractometer, $CuK\alpha$ radiation), and pH titration of solutions on an OP-208 Radelkis precision digital pH meter.

Analysis for potassium and ammonium was performed qualitatively with sodium tetraphenylborate. The other elements were determined quantitatively. Aluminum was determined via back titration of excess Trilon B with zinc nitrate using Xylenol Orange in an urotropine buffer; magnesium was determined complexometrically with Eriochrome Black in an ammonia buffer, masking aluminum with triethanolamine chloride; and copper was determined volumetrically with Trilon B and Xylenol Orange in an urotropine buffer, masking aluminum and magnesium with ammonium fluoride. Vanadium was determined via titration with Mohr's salt solution in the presence of phenylanthranilic acid as an indicator; molybdenum was determined gravimetrically with α -benzoinoxime; and tungsten, niobium, and tantalum were determined gravimetrically after the acidic hydrolysis of samples (WO_3 , Nb_2O_5 , and Ta_2O_5 gravimetric forms).

RESULTS AND DISCUSSION

Figure 1 shows the curves of potentiometric titration of magnesium, copper, and aluminum nitrates

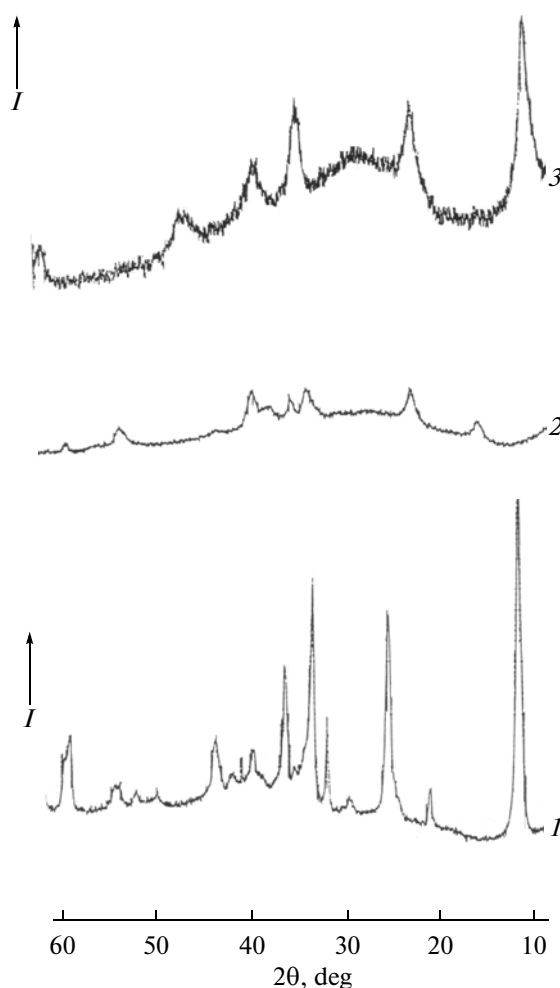


Fig. 2. X-ray diffraction patterns of (1) copper hydroxonitrate $Cu_2(OH)_3NO_3$, (2) copper hydroxide $Cu(OH)_2$, and (3) hydrotalcite-like ternary magnesium copper aluminum hydroxonitrate $[AlMg_{1.9}Cu_{0.125}(OH)_{6.05}][NO_3] \cdot nH_2O$.

and their mixtures with a potassium hydroxide solution. Copper was found to precipitate at pH 4.5–5.5 in the form of well-crystallized basic nitrate $Cu_2(OH)_3(NO_3)$ [13] (Figs. 1, 2; curves 1), aluminum precipitated at pH 3.5–4.5 in the form of an X-ray amorphous hydroxonitrate of variable composition $Al(OH)_n(NO_3)_{3-n} \cdot mH_2O$ (Fig. 1, curve 2) [1], and magnesium precipitated at pH 9.7–10.5 in the form of well-crystallized magnesium hydroxonitrate $MgOHNO_3 \cdot nH_2O$ [1]. From a solution containing copper and magnesium nitrates, two phases precipitated: crystalline $Cu(OH)_2$ at pH 4.7–5.5 [14] (Fig. 1, curve 3; Fig. 2, curve 2) and X-ray amorphous magnesium hydroxonitrate at pH 9.7–10.5. As is established in our earlier work [1], a hydrotalcite-like variable-composition hydroxonitrate $[Mg_nAl(OH)_{2n-2}NO_3] \cdot mH_2O$, which is isomorphous to natural hydrotalcite and crystallizes in hexagonal symmetry with the unit cell parameters $a = 3.02 \text{ \AA}$ and $c = 15.2 \text{ \AA}$, precipitates from magnesium and aluminum nitrate solution at

Table 1. Copper-containing isomorphous hydrotalcite-like mixtures of salts that are alkane oxidative dehydrogenation catalyst precursors

No.	Precursor composition
1	$[\text{AlMg}_{1.9}\text{Cu}_{0.125}(\text{OH})_{6.05}][(\text{CO}_3)_{0.425}(\text{V}_{10}\text{O}_{28})_{0.025} \cdot n\text{H}_2\text{O}]$
2	$[\text{AlMg}_{1.7}\text{Cu}_{0.02}(\text{OH})_{5.44}][(\text{CO}_3)_{0.425}(\text{V}_{10}\text{O}_{28})_{0.005}(\text{Mo}_7\text{O}_{24})_{0.02} \cdot n\text{H}_2\text{O}]$
3	$[\text{AlMg}_{1.71}\text{Cu}_{0.02}(\text{OH})_{5.46}][(\text{CO}_3)_{0.419}(\text{V}_{10}\text{O}_{28})_{0.005}(\text{Mo}_7\text{O}_{24})_{0.02}(\text{H}_2\text{W}_{12}\text{O}_{40})_{0.002} \cdot n\text{H}_2\text{O}]$
4	$[\text{AlMg}_{1.7}\text{Cu}_{0.03}(\text{OH})_{5.6}][(\text{CO}_3)_{0.411}(\text{V}_{10}\text{O}_{28})_{0.005}(\text{Mo}_7\text{O}_{24})_{0.02}(\text{Ta}_5\text{O}_{16})_{0.004} \cdot n\text{H}_2\text{O}]$
5	$[\text{AlMg}_{1.64}\text{Cu}_{0.02}(\text{OH})_{5.32}][(\text{CO}_3)_{0.425}(\text{V}_{10}\text{O}_{28})_{0.005}(\text{Mo}_7\text{O}_{24})_{0.016}(\text{Nb}_6\text{O}_{19})_{0.003} \cdot n\text{H}_2\text{O}]$

Table 2. Initial isomorphous hydrotalcite-like hydroxosalts used to prepare alkane oxidative dehydrogenation catalyst precursors by mixing at a weight ratio of 1 : 1 (see Table 1, nos. 4, 5)

No.	Hydroxosalt that contains niobium or tantalum	Hydroxosalt that does not contain niobium or tantalum
1	$[\text{AlMg}_{1.64}\text{Cu}_{0.02}(\text{OH})_{5.32}][(\text{CO}_3)_{0.476}(\text{Nb}_6\text{O}_{19})_{0.006} \cdot n\text{H}_2\text{O}]$	$[\text{AlMg}_{1.64}\text{Cu}_{0.02}(\text{OH})_{5.32}] \cdot [(\text{CO}_3)_{0.374}(\text{V}_{10}\text{O}_{28})_{0.014}(\text{Mo}_7\text{O}_{24})_{0.032} \cdot n\text{H}_2\text{O}]$
2	$[\text{AlMg}_{1.77}\text{Cu}_{0.03}(\text{OH})_{5.6}][(\text{CO}_3)_{0.472}(\text{Ta}_5\text{O}_{16})_{0.008} \cdot n\text{H}_2\text{O}]$	$[\text{AlMg}_{1.77}\text{Cu}_{0.03}(\text{OH})_{5.6}] \cdot [(\text{CO}_3)_{0.35}(\text{V}_{10}\text{O}_{28})_{0.01}(\text{Mo}_7\text{O}_{24})_{0.04} \cdot n\text{H}_2\text{O}]$

pH 8–9. When a (KOH + K₂CO₃) solution is used as a precipitant, magnesium aluminum hydroxocarbonate, isomorphous to the hydroxonitrate, is crystallized.

The titration curve of nitrate solutions containing magnesium, copper, and aluminum features three plateaus at pH of 3.5–4.5, 4.5–5.5, and 8.5–9.5; these plateaus correspond to the precipitation of aluminum, copper, and hydrotalcite-like magnesium copper aluminum hydroxonitrate, which crystallizes in hexagonal symmetry with the unit cell parameters $a = 3.0 \text{ \AA}$ and $c = 15.5 \text{ \AA}$ (Fig. 1, curve 4; Fig. 2, curve 3). When a potassium hydroxide and carbonate solution is used, a ternary hydroxocarbonate, isomorphous to the hydroxonitrate, precipitates under these conditions. In addition to ternary hydrotalcite-like hydroxonitrate (or hydroxocarbonate), an amorphous halo with the peak $d = 3.2 \text{ \AA}$ (which evidently corresponds to amorphous aluminum hydroxonitrate) is observed in the X-ray diffraction pattern of the precipitate obtained from a solution of the nitrates of three elements.

To clarify the effect of copper(II) on the catalytic activity of oxide catalysts in the oxidative dehydrogenation of alkanes, we prepared copper-containing hydrotalcite-like hydroxosalts with different anions in their interlayer spaces. For this purpose, we synthesized the ternary magnesium copper aluminum hydroxosalt and doped it with decavanadate ion (Table 1, no. 1), decavanadate and paramolybdate ions (Table 1, no. 2), and decavanadate, paramolybdate, and metatungstate ions (Table 1, no. 3) via anion exchange.

In preparing oxidative dehydrogenation catalyst precursors containing niobium in the form of hexaniobate, tantalum in the form of pentatantalate, and other polyoxometalates (decavanadate, paramolybdate, and metatungstate ions), in view of the fact that the latter substitute for the carbonate ion in the interlayer space

of hydrotalcite-like ternary magnesium copper aluminum hydroxosalt at pH 4.5–5.0, and hexaniobate and pentatantalate substitute for it at pH 13, we had to use a mixture of the following two isomorphous phases: hydrotalcite-like aluminum copper magnesium hexaniobate hydroxocarbonate and aluminum copper magnesium hydroxocarbonate containing decavanadate and paramolybdate ions (Table 2, no. 1), or a mixture of hydrotalcite-like aluminum copper magnesium hydroxocarbonate pentatantalate and aluminum copper magnesium hydroxocarbonate containing decavanadate and paramolybdate ions (Table 1, no. 4 and Table 2, no. 2).

The mentioned mixtures were prepared by stirring two initial hydroxosalts at a weight ratio of 1 : 1 in an aqueous medium at $S : L = 1 : 2$ for 2 h until homogeneity was attained. The mixtures proved to be rather homogeneous, as indicated by the sedimentation character and the chemical analysis of pulp samples taken from the top and bottom of the sedimentation cylinder (Al : Nb, Al : Mo, Al : V, and Al : Ta ratios in these samples were the same).

The compositions of the resulting samples (oxidative dehydrogenation catalyst's precursors) are given in Table 1.

The synthesized samples (Table 1) were subjected to thermal treatment, which consisted in drying a precipitate at 100–120°C to a 40% humidity, pelletizing, and calcining in a muffle in an air flow with a continuous rise in temperature at 100 K/h up to 500°C and then exposure to this temperature for 4–5 h. The catalytic properties of the resulting materials were studied in a quartz flow-through reactor with a catalyst load of 1–2 mL. Air oxygen was used as an oxidant. To maintain isothermicity, the catalyst was mixed with an equal volume of ground quartz. The reaction temperature,

Table 3. Results of the oxidative dehydrogenation of ethane on copper-containing catalysts of different compositions

No.	Catalyst composition	T , °C	Dilution, mol/mol C_2H_6/O_2	Conversion, %	Yield, %	Selectivity, %
1	Cu-Al-Mg-V-O	400	1/0.3	10.5	9.6	91.4
		450	1/0.35	11.3	10.1	91.0
2	Cu-Al-Mg-V-Mo-O	400	1/0.3	12.5	11.2	90.0
		450	1/0.3	13.8	12.5	90.5
3	Cu-Al-Mg-V-Mo-W-O	400	1/0.3	13.5	12.6	94.0
		450	1/0.3	14.7	13.7	92.7
4	Cu-Al-Mg-V-Mo-Ta-O	400	1/0.3	17.5	16.6	95.0
		450	1/0.3	19.6	18.8	94.8
5	Cu-Al-Mg-V-Mo-Nb-O	400	1/0.3	17.6	17.5	97.2
		450	1/0.3	20.0	19.6	95.7

Table 4. Results of the oxidative dehydrogenation of propane on catalysts of different compositions

No.	Catalyst composition	T , °C	Conversion, %	Yield, %	Selectivity, %
1	Cu-Al-Mg-V-Mo-Nb-O (Table 1, no. 5)	500	38.4	14.3	37.3
2	Ni-Al-Mg-V-Mo-O	500	12.5	4.3	36.0
3	Bi-Al-Mg-V-Mo-O	520	20.9	8.0	37.9

the hydrocarbon flow rate, and the hydrocarbon/oxygen ratio in the feed mixture were varied over wide ranges. Reaction products were analyzed by liquid chromatography using a Poparak Q column. The contact gas was analyzed for the unconverted feed hydrocarbon (ethane, propane, or hexane), a dehydrogenation product (ethylene, propylene, hexane), CO_2 , and CO. The results of experiments were used to calculate the conversion of the initial compound, the selectivity of the reaction, and the yield of target products as

Conversion (%) = [converted hydrocarbon (mol)/passed hydrocarbon (mol)] \times 100;

Selectivity (%) = [product hydrocarbon (mol)/converted hydrocarbon (mol)] \times 100; and

Yield (%) = [product hydrocarbon (mol)/passed hydrocarbon (mol)] \times 100.

The oxidative dehydrogenation of ethane, propane, and hexane was performed on the catalysts synthesized from samples 1–5 (Table 1). The results of the oxidative dehydrogenation of ethane are summarized in Table 3. The numbers of the catalysts correspond to the numbers of their precursors (Table 1).

The analysis of the results of catalytic studies shows that the conversion of ethane into ethylene on the copper-containing catalysts occurs with a high selectivity (90–97%) at a low temperature (400–450°C; Table 3).

The complication of the catalyst composition from Cu-Al-Mg-V-O through Cu-Al-Mg-V-Mo-O to Cu-Al-Mg-V-Mo-W-O, Cu-Al-Mg-V-Mo-Ta-O, and Cu-Al-Mg-V-Mo-Nb-O improves the catalytic characteristics, increases conversion from 10.5 to 20%

and selectivity from 90 to 97% (Tables 1, 3), and decreases process temperatures at (400–450°C). The best results were obtained for the Cu-Al-Mg-V-Mo-Nb-O catalyst (Table 3, no. 5).

Catalytic activities in oxidative dehydrogenation of propane on catalysts of different compositions are displayed in Table 4, from which it can be seen that the oxidative dehydrogenation of propane on the copper-containing catalyst is more intense than on the other catalysts.

The oxidative dehydrogenation of hexane on the copper-containing catalyst (Table 1, no. 5) proceeds worse than the oxidative dehydrogenation of ethane and propane, but equally as on the Ni-Al-Mg-V-O catalyst and better than on the Ni-Al-V-O catalyst (Table 5).

We should note that all the studied catalysts (Table 3, nos. 1–5) actively functionated in oxidative dehydrogenation reactions, and their activities and selectivities were not reduced after 50 h of operation.

A comparison of the catalytic properties of catalysts that have similar compositions and contain copper oxide, or niobium oxide, or tantalum oxide in addition to Al-Mg-V, Al-Mg-V-Mo, and Al-Mg-V-Mo-W, shows that the niobium-containing catalysts give the best results in the oxidative dehydrogenation of ethane. The tantalum-containing catalysts have similar properties. The replacement of niobium or tantalum by copper considerably worsens the catalytic properties: the yield of ethylene decreases from 15.4 and 17.1 to 10 and 12.5%, respectively, but high selec-

Table 5. Results of the oxidative dehydrogenation of hexane on catalysts of different compositions

No.	Catalyst composition	T , °C	Conversion, %	Yield, %	Selectivity, %
1	Cu-Al-Mg-V-Mo-Nb-O	550	25	7.5	30.0
2	Ni-Al-Mg-V-O	550	25	7.5	30.0
3	Ni-Al-V-O	460	12.5	5.0	40.0

Table 6. Results of the oxidative dehydrogenation of ethane on nickel- and iron-containing catalysts

No.	Catalyst composition	T , °C	Dilution, mol/mol C_2H_6/O_2	Conversion, %	Yield, %	Selectivity, %
1	Ni-V-Mo-W-Al-Mg-O	550	1/1	6.9	2.65	38.7
2	Fe-V-Mo-W-Al-Mg-O	550	1/0.05	7.45	3.30	44.6

tivities (90.0–91.0%) are yet retained. In the simultaneous presence of copper and niobium or copper and tantalum in the, the yield of ethylene increases up to 19.6 and 18.8% with a selectivity of 95.7 and 94.8%, respectively.

We should note that, on the catalysts that simultaneously contain copper and niobium or copper and tantalum, the oxidative dehydrogenation of ethane proceeds at relatively low temperatures (<500°C) with a high selectivity (95.0–95.7%), whereas on the Ni(Fe)-Al-Mg-V-Mo-W oxide catalysts, this process almost does not proceed at low temperatures (<500°C): ethylene yield is near 3% with a selectivity of 38–45% (see Table 6).

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