

SYNTHESIS OF COBALTATE OF NEODYMIUM AND STUDY OF ITS CATALYTIC ACTIVITY IN THE DECOMPOSITION OF HYDROGEN PEROXIDE

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Recently, the ecological situation in the world has been significantly deteriorating as a result of man-made impact on the environment. The development of the methods of neutralization of volatile toxic compounds as a result of their oxidation to carbon dioxide and water on heterogeneous catalysts is an important task. The most active catalysts for this process are noble metals, but their high cost stimulates the search for cheaper catalytic materials based on the oxides of *d*-metals and complex oxides of *d-f*-metals.

In the present work, the synthesis of precursors of heteronuclear complexes of cobalt and neodymium with carboxylic acids with the general formula $\text{Co}_2\text{Nd}_2(\text{L})_5 \cdot n\text{D} \cdot 4\text{H}_2\text{O}$, where $\text{L} = \text{H}_2\text{C}_2\text{O}_4, \text{H}_6\text{C}_4\text{O}_4$, $\text{D} = \text{Phen}, \text{Py}$, was carried out. Studies of their spectral properties, thermal characteristics, and the influence of ligands on the formation of oxide structures, have been carried out.

The composition of the obtained oxide powders was controlled by X-ray powder diffraction. The catalytic properties of the synthesized samples were studied in the model reactions of the decomposition of an aqueous solution of hydrogen peroxide by the volumetric method under normal conditions. On the Figure 1 is shown the X-ray powder diffraction pattern of oxide powder obtained by heating to 800°C of complex $\text{Co}_2\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ for one hour. The research has established that a complex oxide NdCoO_3 is formed, which crystallizes in the cubic crystal system without extraneous phase inclusions [1].

For the sample obtained by heating to 1000°C of the heterocomplex $\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$, in addition to the main phase of the complex oxide NdCoO_3 , the presence of Nd_2O_3 was recorded. This phenomenon can be explained by different stages of decomposition of these complexes. The oxalate heterocomplex decompose through the step of carbonate formation and the succinate heterocomplex decompose through the step isolation of anhydride, which is cleaved off at lower temperatures.

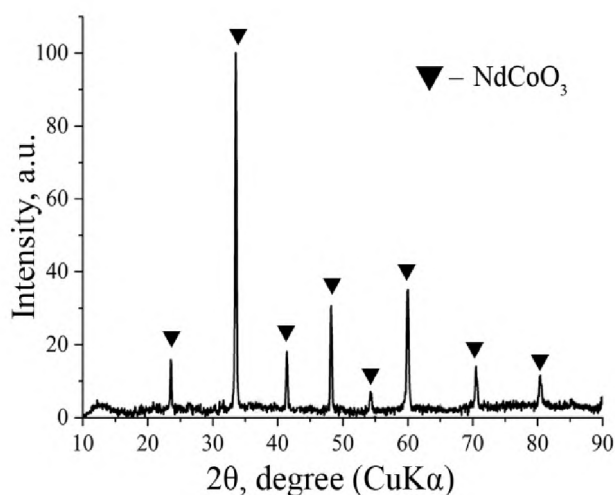


Fig. 1 X-ray powder diffraction patterns of samples, obtained by heating of $\text{Co}_2\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$ at 800°C

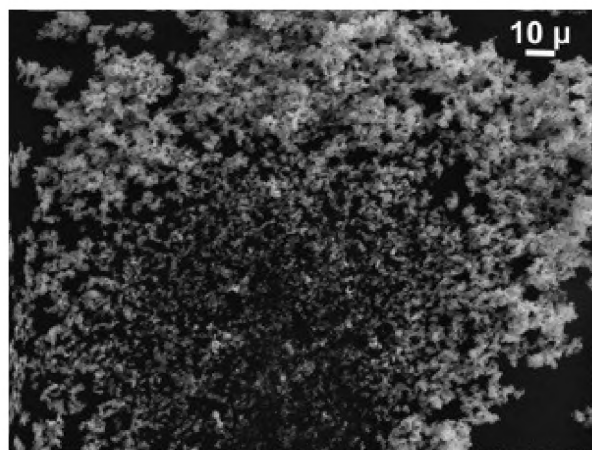


Fig. 2 SEM-image of the synthesized oxide structures, obtained by heating of $\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ at 1000°C

An estimate of the average size of crystallites (d) was given, which was calculated using the Scherer formula [2].

$$d = K \cdot \lambda / (\beta \cdot \cos \theta),$$

where d - average size of crystallites, nm; K - dimensionless factor of the shape of crystallites (Scherer's constant); λ - X-ray wavelength, Å; β - reflection width at half-height of the X-ray peak, θ - diffraction angle.

The average size of crystallites for NdCoO_3 obtained from $\text{Co}_2\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ (800°C) is 24.7–49.9 nm; obtained from $\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ (1000°C) is 28.28–39.57 nm [3]. On the Figure 2 is shown SEM - image of the synthesized oxide structures, obtained by heating the oxalate complex.

To evaluate the effectiveness of the catalytic action of the complex oxide NdCoO_3 , obtained by heating of the heterometallic compounds $\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot n\text{D} \cdot 4\text{H}_2\text{O}$, $\text{Co}_2\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot n\text{D} \cdot 4\text{H}_2\text{O}$, its effect on the rate of decomposition of hydrogen peroxide, was compared. In the Table is presented the rate constants of reactions decomposition of hydrogen peroxide with the participation of the catalyst NdCoO_3 .

Table

Rate constants of reactions decomposition of hydrogen peroxide with the participation of the catalyst NdCoO_3 , obtained by heating the heterometallic compounds

	sample, from which NdCoO_3 is obtained	k , c^{-1} , 3% H_2O_2	k , c^{-1} , 10% H_2O_2
1.	$\text{Co}_2\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ (800°C)	0,005324	0,009199
2.	$\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen} \cdot 4\text{H}_2\text{O}$ (1000°C)	0,004381	0,006224

It is shown that in the experiments conducted with different starting concentrations of hydrogen peroxide, complex oxides show a rather high catalytic activity. The preferable catalytic activity in the reaction of decomposition of hydrogen peroxide, was found for the complex oxide cobaltate of neodymium, obtained by heating the succinate complex with phenanthroline at 800°C .

1. Match! – Phase Identification from Powder Diffraction. Crystal Impact, version 3: manual. – Dr.H. Putz and Dr.K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, 2020. 143p. <http://www.crystalimpact.com/match>.

2. Hammond C. The Basics of Crystallography and Diffraction. - Oxford University Press, 2015, ed.4. 539 p. doi:10.1093/acprof:oso/9780198738671.001.0001.

3. Holland T., Redfern S. Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*. 1997. **61**(404): 65–77.