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## Causes of Non-Additivity Effects in Ni<sup>II</sup> and Co<sup>II</sup> Containing Catalytic Oxidation Systems of Na<sub>2</sub>S by Oxygen

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### Abstract

Positive and negative effects of non-additivity of oxygen absorption rates at oxidation of Na<sub>2</sub>S in the presence (Ni<sup>II</sup> + Co<sup>II</sup>) containing catalysts were detected. It was determined that these effects were associated with peculiarities of the formation of nickel and cobalt sulphides particles. Positive effects of non-additivity were observed in the beginning of the reaction at the stage of forming metals sulphides embryos and referred to synergistic phenomena. Negative effects were detected at the growth stage of the sulphide phase particles. They are of nonsynergistic nature and associated with deposition of nickel sulphides on the surface of cobalt sulphide particles..

**Key words:** non-additivity, catalysis, oxidation, nickel sulphide, cobalt sulphide

### INTRODUCTION

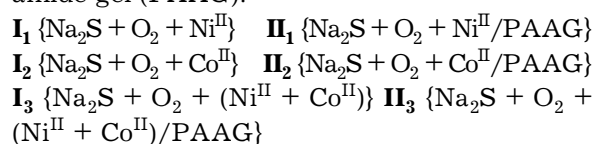
Non-additivity effects are widely circulated in catalysis [1–6]. They are often called synergies effects. The diversity of such phenomena was described in Golodov's work and their classification on the nature of emergence was proposed [1]. However, not always phenomena of nonadditivity can be referred to effects of precisely synergies interpreted as the concerted joint action of the catalytic system components, *e. g.* the catalyst components [3]. The nonsynergistic nature of nonadditivity effects takes places in systems, where catalyst components interacting between each other form new chemical compounds that are stable complexes, clusters, associates *etc.* [4, 5]. The effects of nonadditivity emerging due to the interaction of catalysts with the reaction medium that may lead to a change in the phase state of catalysts during the reaction could also be referred here.

One of such examples is the reaction system Na<sub>2</sub>S–O<sub>2</sub> – transition metal ions. It is interesting by the fact that oxidation of S<sup>2-</sup> by oxygen occurs under conditions of the con-

tinuous formation of the catalytically active phase that is metal sulphides [6]; on the other hand, when introducing in such systems the second metal ions non-additivity effects of the catalytic action of such binary catalysts that are referred precisely to synergistic effects are noted [3]. But non-additive oxide adsorption in such systems may be associated with and with the processes of a change in the phase state of the catalyst during substrate oxidation.

Therefore, the range of issues that the authors were interested in included the relationship between the causes, nature (magnitude, sign) of the non-additivity effects and processes of the formation of the sulphide phase at Na<sub>2</sub>S oxidation in the presence of binary catalysts.

Catalytic systems of two types were studied in the work: systems **I** with loose metal ions and systems **II** with metal ions introduced in a three-dimensional polymer grid of polyacrylamide gel (PAAG):



## EXPERIMENTAL

Ch. d. a. (pure for analysis) reagent grade  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , acrylamide (AA), *N,N'*-methylene-bis-acrylamide (BAA), as well as technical oxygen with the volume fraction of oxygen of no less than 99.7% were used in the work.

PAAG with a cross-linking degree of 2 mass % and the swelling capacity of (20+2) g  $\text{H}_2\text{O}/\text{g}$  of polymer was obtained by a radical polymerization method using BAA as a crosslinking agent [7]. AA and BAA were preliminarily recrystallized from ethanol.

Catalysts were prepared from 0.01 M solutions of  $\text{NaCl}_2$  and  $\text{CoCl}_2$ . In  $\mathbf{I}_1$ – $\mathbf{I}_3$  systems,  $\text{Na}_2\text{S}$  oxidation was performed in the presence of 0.2 mL of solutions of  $\text{CoCl}_2$  or  $\text{NiCl}_2 + \text{CoCl}_2$ . Herewith, the content of metal ions in  $\mathbf{I}_1$ – $\mathbf{I}_2$  systems in experiments was varied from  $0.4 \cdot 10^{-6}$  mol (20%) to  $2 \cdot 10^{-6}$  mol (100%). The initial 0.01 M solutions of  $\text{NiCl}_2$  and  $\text{CoCl}_2$  in  $\mathbf{I}_3$  system were mixed in the percentage ratios of 20/80, 40/60, 60/40 and 80/20 by preserving constant the total number of metal ions, equal to  $2 \cdot 10^{-6}$  mol.

Catalysts for  $\mathbf{II}_1$ – $\mathbf{II}_3$  systems were prepared by the impregnation method. To 0.0092 g of air-dry PAAG, 0.2 mL of a solution of  $\text{NiCl}_2$  or  $\text{CoCl}_2$  or a mixture of these salts in the required proportion were flown. Herewith, the entire added solution passed into the phase gel, and extremely swollen samples of catalysts were obtained. Varying the relative content of metal ions in catalyst of systems  $\mathbf{II}_1$ – $\mathbf{II}_3$  was carried out analogously to appropriate systems  $\mathbf{I}_1$ – $\mathbf{I}_3$ .

The system catalytic activity was determined by the volumetric method in a static system at the atmospheric pressure in the excess of  $\text{O}_2$  and a temperature of  $(40 \pm 0.05)^\circ\text{C}$ , according to the technique described in work [8]. In one compartment of the reactor, 5 mL of a 0.1 M aqueous solution of  $\text{Na}_2\text{S}$  was loaded, in the second compartment – a catalyst. The reactor was connected to oxygen and intense stirring the system in a high-speed rocker by registering  $\text{O}_2$  adsorption through certain time intervals.

The measured volumes of adsorbed  $\text{O}_2$  were brought to normal conditions and curves of  $\text{O}_2$  consumption from time were constructed, after differentiation of which

initial ( $W_0$ ) and maximum ( $W_{\text{max}}$ ) absorption rates of  $\text{O}_2$  were determined. Based on them, the catalytic activity  $a$  (in  $\text{mol O}_2/(\text{s} \cdot \text{mol M}^{\text{II}})$ ) according to the formula

$$a = W/n \cdot 60 \cdot 22400$$

where  $W$  is the current rate of  $\text{O}_2$ ,  $n$  is the number of moles of  $\text{Ni}^{\text{II}}$  and/or  $\text{Co}^{\text{II}}$  in the experiment.

The behaviour of binary catalysts in the oxidation process of  $\text{Na}_2\text{S}$  was studied in systems  $\mathbf{I}_3$  and  $\mathbf{II}_3$  by determining in them adsorption rates ( $W_{\text{n/add}}$ ) of  $\text{O}_2$  at various relative contents of  $\text{Ni}^{\text{II}}$  and  $\text{Co}^{\text{II}}$ . Concentration dependencies  $W_0$  and  $W_{\text{max}}$  of  $\text{O}_2$  adsorption in all systems were constructed according to appropriate kinetic data.

Values of additive rates ( $W_{\text{add}}$ ) were calculated from data obtained for systems  $\mathbf{I}_1$  and  $\mathbf{I}_2$  or  $\mathbf{II}_1$  and  $\mathbf{II}_2$  by addition of appropriate concentration dependencies of  $\text{O}_2$  consumption rates in these systems.

The value of the non-additivity effect ( $\Xi$ ) was calculated according to the formula

$$\Xi = (W_{\text{n/add}} - W_{\text{add}})/W_{\text{add}} = (W_{\text{n/add}}/W_{\text{add}}) - 1$$

The study of catalysts was carried out by the method of ESR spectroscopy. One did not manage to extract the sulphide phase of catalysts from systems  $\mathbf{I}$  due to its high dispersity, therefore, polymer containing catalysts were studied. ESR spectra were registered using a Radiopan SE/X-2542 radiospectrometer with the operating frequency of 9.4 GHz. Magnetic field calibration was performed using a nuclear magnetometer. The signal of *N,N*-diphenyl-*N'*-picrylhydrazyl (DPPH) was applied for determining the  $g$ -factor. All measurements were performed at 77 K.

## RESULTS AND DISCUSSION

Kinetic dependencies of volumes of  $\text{O}_2$  adsorbed in the course of the reaction in all catalytic systems had the S-shaped form. Such a shape of curves is associated with a set of physicochemical changes of catalysts caused by their interaction with the reaction medium and including both a change in the composition and structure of active sites of catalysts, and properly phase formation processes. According to [9], the formation of a new phase proceeds

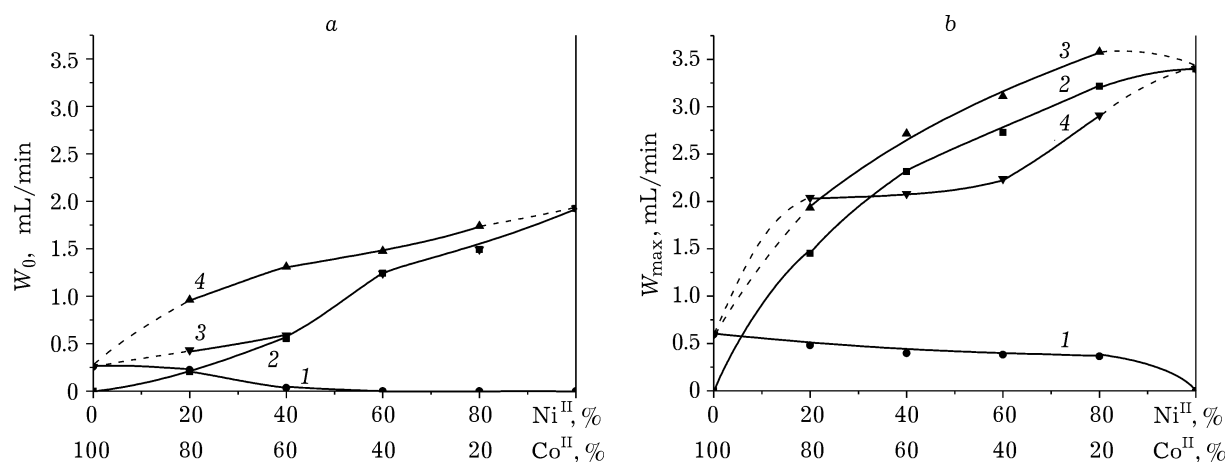


Fig. 1. Initial rates ( $W_0$ ) (a) and maximum rates ( $W_{max}$ ) (b) of O<sub>2</sub> adsorption in the oxidation process of Na<sub>2</sub>S in the presence of: Co<sup>II</sup> (1), Ni<sup>II</sup> (2), Co<sup>II</sup> + Ni<sup>II</sup> (3 and 4) (3 - calculated, 4 - experimental). Here and in Figs. 2, 3: 100 % corresponds to  $2 \cdot 10^{-6}$  mol of metal ions in the experiment.

via the emergence and the growth of its embryos. In the beginning of the reaction, when embryos of the solid product are virtually absent, the rate of the catalytic reaction is quite low. With the appearance of embryos, and consequently, phase interface, the reaction rate is increased, proceeds through the maximum at reaching the maximum interface and then is decreased as the consolidation of the particle phase.

Due to the S-shaped form of all kinetic curves, their processing was conducted according to initial  $W_0$  and maximum  $W_{max}$  values of adsorption rates of O<sub>2</sub> for each system. Concentration dependencies  $W_0$  and  $W_{max}$  for system I<sub>1</sub>-I<sub>3</sub> are presented in Fig. 1, a and b, respectively. Since  $W_0$  values in systems II<sub>1</sub>-II<sub>3</sub>

were practically equal to zero, only concentration dependencies  $W_{max}$  were constructed for these systems (Fig. 2).

Curves 1 and 2 in Fig. 1, a and b indicate that nickel catalysts without PAAG are several times more active than appropriate cobalt analogs when assessing both by  $W_0$  and  $W_{max}$ . At the same time, the shape time of concentration curves do not depend on the nature of metal ions, which may reflect total regularities of the formation of nickel and cobalt sulphides under conditions of catalysis.

The beginning of the reaction of Na<sub>2</sub>S oxidation that is characterized by  $W_0$  values obviously coincides with the processes of the emergence and the growth of the sulphide phase. The number of embryos is the more, the greater the content of metal ion in the system. Owing to high dispersity of the active phase at this stage, the majority of sulphide centers appear to be available for the oxidizable substrate, and the catalyst activity should remain constant at the condition of the unchanged activity of each centre and the linear growth of their number when increasing the number of the metal ion. The activity growth of Ni<sup>II</sup> and Co<sup>II</sup> containing catalysts observable in Fig. 3, a (curves 2, 4) can be conditioned by a linear dependence of the embryos number on the concentration of the metal ion and/or a change in the composition, structure, and, consequently, and the activity of catalysis centres with an increase in the content of the metal ion.

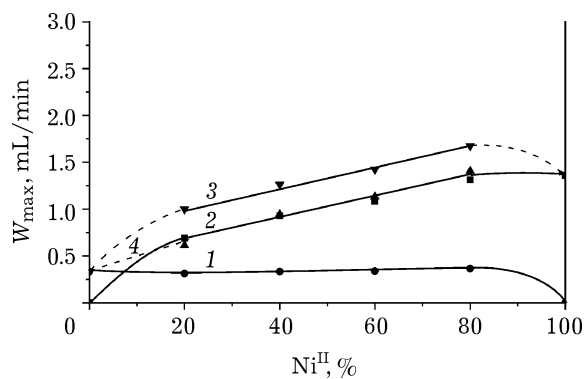


Fig. 2. Maximum rates ( $W_{max}$ ) of O<sub>2</sub> adsorption in the oxidation process of Na<sub>2</sub>S in the presence of: Co<sup>II</sup>/PAAG (1), Ni<sup>II</sup>/PAAG (2), (Co<sup>II</sup> + Ni<sup>II</sup>)/PAAG (3 and 4) (3 - calculated, 4 - experimental).

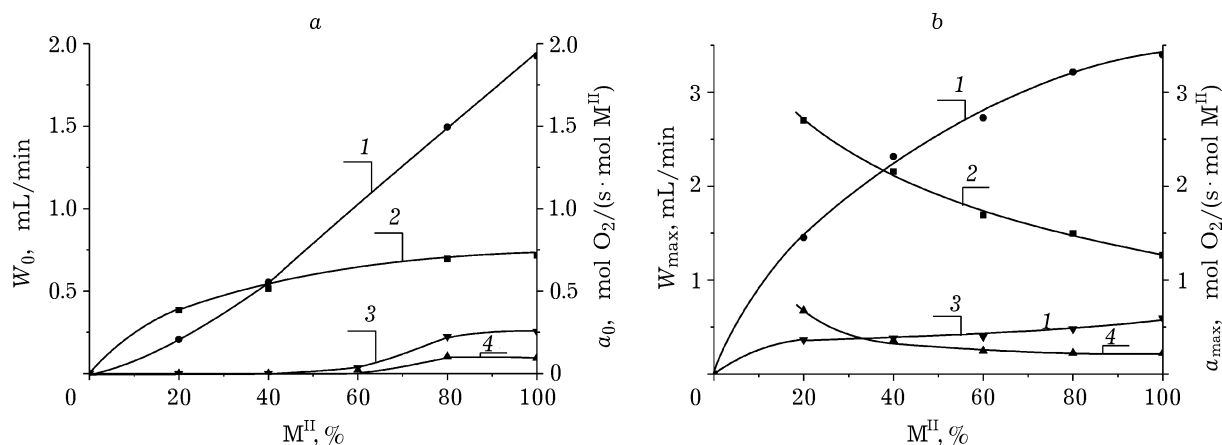


Fig. 3. Initial rates ( $W_0$ ) (a) and maximum rates ( $W_{\max}$ ) (b) and maximum activities ( $a_{\max}$ ) (2, 4) of  $O_2$  adsorption during oxidation of  $Na_2S$  in the presence of  $Ni^{II}$  (1, 2) and  $Co^{II}$  (3, 4).

During the period of achieving  $W_{\max}$ , slope opposition of concentration dependencies of the total and the specific consumption rates of  $O_2$  in this process is observed (see Fig. 3, b). Apparently, this is due to the fact that a part of active centers of catalysts goes into the sulphide phase volume and becomes inaccessible for the oxidizable substrate. Therefore, formal decreasing the activity of both  $Ni^{II}$  and  $Co^{II}$  containing catalysts represents a trivial fact of the effect of the dispersity degree in heterogeneous catalysts on their activity.

Concentration dependencies of experimental (non-additive) values  $W_0$  and  $W_{\max}$  for binary catalysts (**I**<sub>3</sub> systems) are presented by curves 4, and dependencies of calculated (additive) values corresponding to them – by curves 3 (see Fig. 1, a and b). Misalignment of curves 3 and 4 testifies the availability of a non-additivity effect in the systems under study

TABLE 1

Value of non-additivity effect ( $\Xi$ ) calculated according to initial ( $\Xi_{W_0}$ ) and maximum ( $\Xi_{W_{\max}}$ ) oxidation rates of  $Na_2S$  for various partial contents of  $Ni^{II}$  and  $Co^{II}$  in catalysts

Ni <sup>II</sup> /Co <sup>II</sup> , %	Systems		
	<b>I</b> <sub>3</sub>	<b>II</b> <sub>3</sub>	
	$\Xi_{W_0}$	$\Xi_{W_{\max}}$	$\Xi_{W_{\max}}$
20/80	1.2	0	-0.4
40/60	1.2	-0.4	-0.3
60/40	0.2	-0.3	-0.2
80/20	0.2	-0.2	-0.2

both at  $W_0$  and at  $W_{\max}$ . Herewith, the positive effect of non-additivity in the systems under study is observed at the initial stage of the reaction, and in the period of achieving  $W_{\max}$ , it is negative (Table 1).

The introduction of metal ions into a polymer matrix (systems **II**) leads to slowing substrate oxidation rates in comparison with systems **I**. Obviously, this is associated with the appearance of diffusional difficulties and accordingly, slowing the processes of forming the active catalyst phase flowing during the reaction [7, 8]. Herewith, it turned out that  $W_0$  values in case of supported catalysts decreased to zero. This did not allow assessing the value and the sign of a non-additivity effect in systems **II** at the initial stage of the reaction,  $W_{\max}$  for these systems were on average in two times lower than appropriate values for systems **I**. The results of processing kinetic curves at the period of achieving  $W_{\max}$  in systems **II**<sub>1</sub>–**II**<sub>3</sub> are given in Fig. 2 and Table 1. As follows from Table 1, in the period of achieving  $W_{\max}$  in systems **I**<sub>3</sub> and **II**<sub>3</sub> non-additivity effects practically equal by value sign appear. This testifies that the polymer matrix does not exert a noticeable effect on causes of a non-additivity effect and its sign.

According to Fig. 2, in systems with  $Co^{II}$ /PPAG (curve 1),  $W_{\max}$  slightly depends on the content in them of cobalt ions, and binary ( $Ni^{II}$  +  $Co^{II}$ /PAAG) catalyst (curve 3) behaves as multicomponent  $Ni^{II}$ /PAAG (curve 2). This causes the appearance of the negative effect

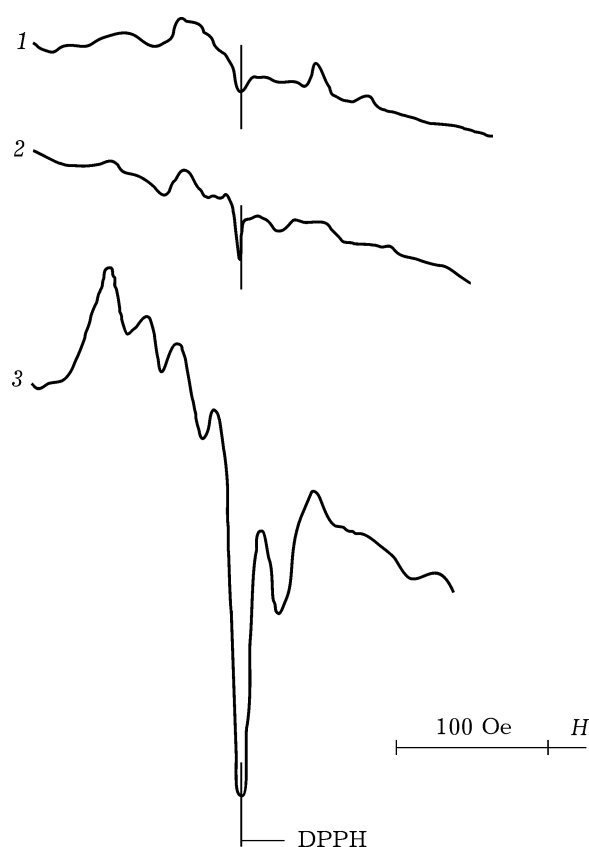


Fig. 4. EPR spectra of Co<sup>II</sup>/PAAG at various process stages: 1 – before catalysis; 2 – during the period of reaching  $W_0$ ; 3 – during the period of reaching  $W_{max}$ .  $T = 77$  K.

of non-additivity in the whole range of Ni<sup>II</sup> and Co<sup>II</sup> ratios. The most probable reason of this behaviour of (Ni<sup>II</sup> + Co<sup>II</sup>/PAAG) catalyst is the isolation of its cobalt containing active centres due to different formation rates and the growth of embryos of nickel and cobalt sulphides. One may suggest that nickel sulphides are formed on cobalt sulphide particles by avoiding contact of the latter with the reaction medium.

This suggestion is confirmed by the appearance of the ESR signal for Co/PAAG samples in the period of achieving  $W_{max}$  (Fig. 4) that is absent in case of binary (Ni<sup>II</sup> + Co<sup>II</sup>/PAAG) catalysts. This signal can be attributed to the formation of a monoadduct of Co<sup>II</sup> with O<sub>2</sub> ( $\mu$ -superoxide complex) described in the literature [10, 11]:  

$$\text{Co(L)} + \text{O}_2 \leftrightarrow \text{Co(L)} \cdot (\text{O}_2)$$
 where L is ligand.

The displacement of the electron density from cobalt ion to oxygen occurs in the adduct, cobalt ion formally changes the valence Co<sup>II</sup> → Co<sup>III</sup>, and O<sub>2</sub> ion radical is formed. The appear-

ance of the latter leads to the emergence of the ESR signal in the spectrum of the Co<sup>II</sup> containing catalyst (see Fig. 4, spectrum 3).

Values of the parameter  $g_{\perp}$  for various Co<sup>II</sup> compounds and their adducts with O<sub>2</sub> are presented in Table 2. From it one can see that values of the  $g_{\perp}$  parameter of cobalt compounds before and after the formation of adduct with O<sub>2</sub> differs greatly. In the latter case, they are lower and vary near the value of 2000. The value  $g_{\perp} = 2.002$  obtained in the present work testify in favour of the formation of a cobalt-oxygen monoadduct during the reaction. And the closeness of the calculated values of the parameters  $g_{\perp} = 2.002$  and  $g_{\parallel} = 2.006$  is apparently triggered by pulling almost all the electron density (~90 %) away from Co<sup>II</sup> to oxygen [11]. The absence of a similar signal in ESR spectra of binary catalysts indicates the fact that Co<sup>II</sup> ions in this case do not interact with oxygen, obviously due to their isolation under a sulphide nickel layer.

## CONCLUSION

Thus, formation processes of nickel and cobalt sulphides exert influence on non-additive effects of oxygen adsorption during Na<sub>2</sub>S oxidation in the presence of binary catalysts. In the beginning of the reaction at the stage of the emergence of the phase embryos, positive effects of non-additivity arise; the latter, apparently, may be referred to synergetic phe-

TABLE 2

EPR spectral parameters of Co<sup>II</sup> compounds and their monoadducts with oxygen [11]

Compounds	Value of parameter $g_{\perp}$	
	Without O	Adduct with O <sub>2</sub>
Co(Salen)(DMSO)	2.500	1.998
Co(Salen)(THF)	2.409	1.999
Co(Salen)(Py)	2.354	1.999
Co(Pc)(Py)	2.327	2.004
Co(Hdmg) <sub>2</sub> (Py)	2.240	2.000

Note. Salen – N,N'-ethylene-bis(salicylideneimine), DMSO – dimethyl sulphoxide, THF – tetrahydrofuran, Py – pyridine, Pc – phthalocyanine, Hdmg – dimethylglyoxime.

nomena. Negative effects noted at the growth stage of particles of the sulphide phase are not associated with synergism, since a bicomponent catalyst containing ( $\text{Ni}^{\text{II}} + \text{Co}^{\text{II}}$ ) operates at this stage as a multicomponent nickel due to deposition of nickel sulphides on the surface of  $\text{Co}^{\text{II}}$  containing particles. Therefore, possible non-additivity effects in the system, where alongside with a catalytic reaction, there is a change in the phase condition of a catalyst, may be of non-synergistic nature conditioned precisely by peculiarities of phase transformations of catalysts.

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