

UDC 544.723

## COMPENSATION EFFECT ON Cu-Co-Fe OXIDE CATALYSTS OF CO OXIDATION

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*The occurrence of compensation effect on massive and supported oxide catalysts of CO oxidation is shown. The explanation of compensation effect is offered based on the data on the surface state of the catalysts that are obtained by means of thermally programmed desorption method with mass spectrometric registration of the desorbed particles (TPD MS).*

### INTRODUCTION

The interest to CO oxidation reaction does not become weaker last time due to the importance of this reaction for Green chemistry. However, one can not forget that this reaction is the convenient model process for investigation of peculiarities of the heterogeneous catalysis. The compensation effect is one of the interesting effects that are observed in catalysis. It does not possess an unambiguous explanation. Several explanations of its occurrence can be found in literature and the next ones are the most widespread.

#### 1. Enthalpy-entropy relationship.

If the linear relationship between the activation enthalpy and entropy takes place for the series of similar reactions, then because of the facts that activation entropy enters into the pre-exponential factor and activation enthalpy enters into the activation energy, the compensation relation (linear relation between the logarithm of the pre-exponential factor and the activation energy) is to be expected [1, 2]

$$k = \frac{\kappa T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) = k_0 \exp\left(-\frac{E}{RT}\right), \quad (1)$$

$$\Delta H^* = a + b\Delta S^* \Rightarrow \ln k_0 = a' + b'E. \quad (2)$$

#### 2. The activation energy distribution of active sites.

In the case when reaction has different activation energies on different active sites:

$k_i = n_i k_0 \exp(-E_i/RT)$  where  $n_i$  – quantity of active sites of  $i$ -th type,  $E_i$  – activation energy for the reaction on these sites, and the distribution function  $n_i = f(E_i)$  has the exponential form and

its parameters differ from sample to sample, the apparent values of activation energies and pre-exponential factors will be related by compensation relation [3].

3. If (a) the reaction kinetics is described by one rate-limiting step and it is possible to write an expression  $k = \alpha k_0 \exp(-E/RT)$  where  $k_0$  and  $E$  are constants and refer to the rate-limiting step and  $\alpha$  is the temperature-dependent parameter that expresses the possibility of the occurrence of this step, and (b) the temperature dependency of  $\alpha$  differs from sample to sample, the compensation effect is observed [4]. E.g.,  $\alpha$  can meet the surface concentration of the reagent in the adsorption equilibrium and the relation of  $\alpha$  to temperature is described, through the equilibrium constant of adsorption, by the standard equation of type  $\alpha = a \exp(-\Delta G^0/RT)$ . By turn,  $\Delta G^0$  can differ from sample to sample and this leads to the compensation behavior.

4. Compensation effect can take place if the concentration of adsorbate is described by the power law with variable kinetic order by reagent pressure [5].

5. Authors [6] attribute the compensation effect solely to the change in the kinetic equation from sample to sample, in particular in the case of power law. It is believed that if the kinetic equation is the same for all the samples in the series, no compensation effect should be observed. Hence, the compensation effect is "apparent" and does not require any special explanation.

In the series of recent works of our laboratory [7–22] oxide systems based on Cu, Co and Fe were studied in the reaction of CO oxidation. The data on catalytic activity of studied catalysts are presented in the mentioned papers. In the present work the existence of compensation effect over

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such catalysts is ascertained and the explanation is given based on the catalysis and TPD of the reaction product data.

### EXPERIMENTAL

Catalytic studies of CO oxidation were conducted in the straight-flow reactor with 8 mm inner diameter in the gaseous mixture that contained 2% CO and 20% O<sub>2</sub> with flow of 100 cm<sup>3</sup>/min. Sample weights were 0.5–1.0 g. Temperature of full CO conversion (*t*<sup>100</sup>) was taken as the measure of catalytic activity.

The next series of samples were investigated:

1) massive samples that consist of binary oxide systems Fe–Co [7], Cu–Co [8], Cu–Fe [9], Fe–Mn [10], the ternary system Cu–Co–Fe with different contents of metals [11–13];

2) samples in which the Cu–Co–Fe ternary oxide system is supported on different supports:

- thermoexfoliated graphite (TEG), TEG modified by hydrogen peroxide and nitric acid [14];

- fruit stone activated carbon (FAC) unmodified and modified by maleic anhydride [15], hydrogen peroxide and nitric acid [16];

- silica gel [17];

- silicon carbide (powdered and nanofibers) unmodified and etched by different acid mixtures [18, 19];

- carbon nanotubes synthesized by means of low-temperature CO conversion on nickel, iron and cobalt oxides [20, 21];

- carbon nanotubes synthesized pyrolytically on iron oxide and nickel oxide catalysts [22].

Kinetic curves in coordinates CO conversion versus temperature, obtained for catalyst in the straight-flow reactor, were linearized in the next coordinates:

$$\ln \ln [1/(1-x)] = \ln VC_0/F + \ln k_0 - E/RT, \quad (3)$$

where *x* – CO conversion, *V* – catalyst bed volume, *C*<sub>0</sub> – CO concentration at the reactor inlet, *F* – CO supply rate, *k*<sub>0</sub> – pre-exponential factor, attributed to unit volume of catalyst bed, *E* – reaction activation energy.

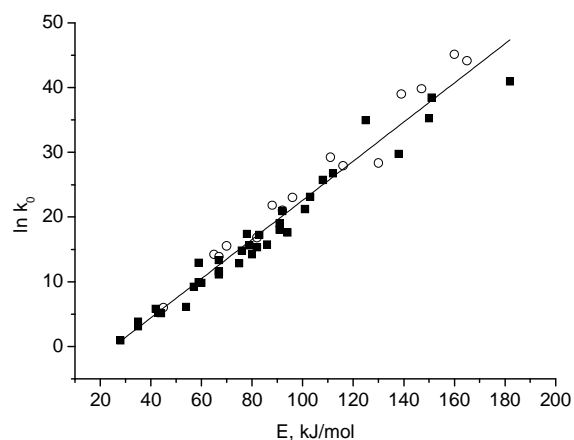
The surface of all samples after catalysis was studied by means of thermally programmed desorption (TPD) with mass spectrometric (MS) detection of the desorbed particles. Samples were placed into the quartz cell attached to the inlet of mass-spectrometer. TPD MS spectra were recorded with a MX7304A mass spectrometer with linear heating law at the rate of 10 K s<sup>-1</sup>.

### RESULTS AND DISCUSSION

Data on composition of the studied catalysts and on values of kinetic parameters of the reaction ( $\ln k_0$ , *E*), calculated by above mentioned method from the data given in [7–22], are presented in Tables 1, 2. Dimension of *k*<sub>0</sub> is 1 cm<sup>-3</sup>·s<sup>-1</sup> and is attributed to unit volume of the catalyst bed.

**Table 1.** Composition of massive catalysts that were synthesized by evaporation of metal nitrates solution with further decomposition to oxides (indices: sample composition, mass. % of metals) and corresponding values of kinetic parameters

Sample	Kinetic parameters	
	$\ln k_0$	<i>E</i> , kJ·mol <sup>-1</sup>
Fe <sub>95</sub> Mn <sub>5</sub>	6.0	45
Fe <sub>30</sub> Mn <sub>70</sub>	21.8	88
Fe <sub>15</sub> Co <sub>85</sub>	15.5	70
Fe <sub>75</sub> Cu <sub>25</sub>	28.3	130
Fe <sub>15</sub> Cu <sub>85</sub>	45.1	160
Cu <sub>5</sub> Co <sub>95</sub>	14.2	65
Cu <sub>95</sub> Co <sub>5</sub>	44.1	165
Cu <sub>94.05</sub> Co <sub>4.95</sub> Fe <sub>1.00</sub>	39.8	147
Cu <sub>93.38</sub> Co <sub>4.94</sub> Fe <sub>1.25</sub>	29.2	111
Cu <sub>4.75</sub> Co <sub>90.25</sub> Fe <sub>5</sub>	27.9	116
Cu <sub>45</sub> Co <sub>45</sub> Fe <sub>10</sub>	13.9	67
Cu <sub>92</sub> Co <sub>3</sub> Fe <sub>5</sub>	16.8	82
Cu <sub>85</sub> Co <sub>10</sub> Fe <sub>5</sub>	23.0	96
Cu <sub>90.25</sub> Co <sub>4.75</sub> Fe <sub>5</sub>	39.0	139
Cu <sub>90.25</sub> Co <sub>4.75</sub> Fe <sub>5</sub> (synthesized from metal carbonates)	21.0	92



**Fig. 1.** The dependence  $\ln k_0 = f(E)$  for massive (○) and supported (■) samples of Cu–Co–Fe oxide systems

**Table 2.** Composition and kinetic parameters for Cu-Co-Fe oxide catalysts of CO oxidation supported on different supports. The amount of active mass is expressed in percents (mass of metals to mass of the support) and is indicated after slash. The active mass of all samples had the fixed ratio of metals:  $\text{Cu}_{90,25}\text{Co}_{4,75}\text{Fe}_5$  and was deposited by impregnation of the support with metal nitrates solution with further evaporation, drying and forming in the reaction mixture. CNT<sub>(Me)</sub> – carbon nanotubes, synthesized on the Me-containing catalyst. Support pre-treatment method is indicated in parentheses

Sample	Kinetic parameters	
	$\ln k_0$	E, $\text{kJ mol}^{-1}$
TEG/57	20.9	92
TEG(disp)/55	14.2	80
FAC/10	15.7	86
FAC/15	9.8	60
FAC(H <sub>2</sub> O <sub>2</sub> )/10	40.9	182
FAC(HNO <sub>3</sub> )/10	18.0	91
SiO <sub>2</sub> /15	3.1	35
SiO <sub>2</sub> /20	5.2	43
SiC/15	17.6	94
SiC/20	3.8	35
SiC(HF+HNO <sub>3</sub> )/25	5.8	42
SiC <sub>nanofibers</sub> /10	6.1	54
SiC <sub>nanofibers</sub> /20	5.1	44
SiC <sub>nanofibers</sub> (HF+HNO <sub>3</sub> )/25	15.6	79
CNT <sup>1</sup> <sub>(Co)</sub> /10	34.9	125
CNT <sup>1</sup> <sub>(Co)</sub> /15	12.9	59
CNT <sup>1</sup> <sub>(Co)</sub> /10+5	9.2	57
CNT <sup>1</sup> <sub>(Fe)</sub> /5+10	11.6	67
CNT <sup>1</sup> <sub>(Fe)</sub> /10+5	0.9	28
CNT <sup>1</sup> <sub>(Fe)</sub> /15	17.4	78
CNT <sup>1</sup> <sub>(Ni)</sub> /25	9.9	59
CNT <sup>1</sup> <sub>(Ni)</sub> /5+10	11.1	67
CNT <sup>1</sup> <sub>(Ni)</sub> /10+5	12.8	75
CNT <sup>1</sup> <sub>(Ni)</sub> /15	14.8	76
CNT <sup>2</sup> <sub>(Fe)</sub> /10	19.0	91
CNT <sup>2</sup> <sub>(Fe)</sub> /20	17.2	83
CNT <sup>2</sup> <sub>(Fe)</sub> /30	26.7	112
CNT <sup>2</sup> <sub>(Fe)</sub> /40	25.7	108
CNT <sup>2</sup> <sub>(Fe)</sub> /50	23.1	103
CNT <sup>2</sup> <sub>(Ni)</sub> /10	15.3	82
CNT <sup>2</sup> <sub>(Ni)</sub> /20	35.2	150
CNT <sup>2</sup> <sub>(Ni)</sub> /30	29.7	138
CNT <sup>2</sup> <sub>(Ni)</sub> /40	38.4	151
CNT <sup>2</sup> <sub>(Ni)</sub> /50	21.2	101
CNT <sup>2</sup> <sub>(Ni)</sub> /20+20	13.3	67

According to the data given in Tables 1, 2, the changes in the activation energy and logarithm of the pre-exponential factor are symbasical. In the coordinates  $\ln k_0$  versus  $E$  all data fit the straight line (Fig. 1).

The slope of the compensation line equals to  $(3.02 \pm 0.09) \cdot 10^{-4} \text{ mol J}^{-1}$  that corresponds to the isokinetic temperature of  $126 \pm 12^\circ\text{C}$  and to CO conversion of 20–30%. Above the isokinetic temperature (in the region of high conversions) samples with higher values of the activation energy show lower temperatures of the same conversion, e.g., lower temperatures of full CO conversion. Thereby, high values of Arrhenius parameters ( $\ln k_0$ ,  $E$ ) are preferable for such oxide systems in the development of low-temperature CO oxidation catalysts.

The compensation effect takes place for all studied oxide catalysts based on Cu, Co, and Fe being not influenced by active mass amount, by active mass composition, by metals and by support type. Hence, this phenomenon has chemical nature and probably connected to method of synthesis and chemical composition of the active mass.

For the series of catalysts the formation of copper hydroxonitrate  $\text{Cu}_2(\text{OH})_3\text{NO}_3$  due to copper nitrate hydrolysis is detected [10–21].

The state of the surface layer for all samples after catalysis was studied by means of TPD MS spectrometry. All catalysts are characterized by desorption of the reaction product  $\text{CO}_2$  in the reasonably narrow temperature interval of 150 to  $250^\circ\text{C}$ . But the calculation of the kinetic parameters of  $\text{CO}_2$  desorption from TPD profile gives the wide scattering of the values of activation energy and the pre-exponential factor and the latter change symbasically from sample to sample. Thus, the compensation effect also takes place for desorption – the process over different samples runs at close temperatures but with significantly different energetics. The compensation line parameters can be estimated from the Eq. (4) [23]

$$v_0 = \frac{\beta}{m(n_s)_M^{m-1}} \frac{E_d}{RT_M^2} \exp\left(\frac{E_d}{RT_M}\right), \quad (4)$$

where  $T_M$  – temperature of the desorption peak maximum,  $E_d$  – activation energy of the desorption,  $v_0$  – pre-exponential factor,  $\beta$  – heating rate,  $n_s$  – surface concentration of the adsorbate,  $m$  – the kinetic order of desorption.

Eq. (4) gives the relationship between activation energy, pre-exponential factor and temperature of desorption. For studied samples  $T_M$  is in the interval 150–250°C. Thus, the probable compensation lines were calculated for the boundaries of this interval (150 and 250°C) and for the intermediate value 200°C from the Eq. (5) (which is the logarithmical form of Eq. (4))

$$\ln v_0 = \text{const} + \ln E_d + \frac{E_d}{RT_M} \quad (5)$$

The calculated lines are shown on the Fig. 2.

The slopes of these lines ( $2.94 \cdot 10^{-4} \text{ mol} \cdot \text{J}^{-1}$  for 150°C and  $2.4 \cdot 10^{-4} \text{ mol} \cdot \text{J}^{-1}$  for 250°C) are in good agreement with the slope of the compensation

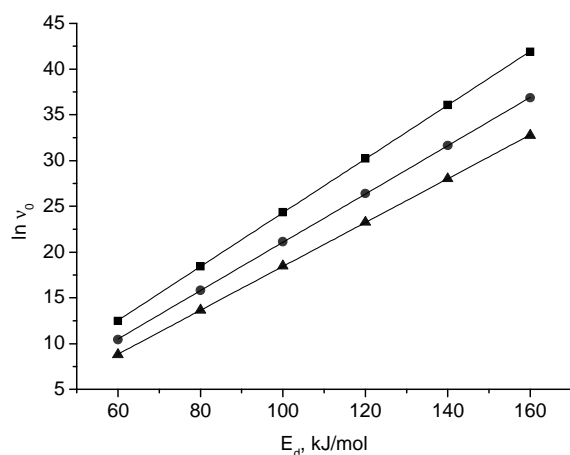
line calculated from the catalytic experiments data. Along with this, the kinetic parameters of CO oxidation reaction and the kinetic parameters of CO<sub>2</sub> desorption from the catalyst surface change symbasically (see Table 3).

Kinetic parameters of CO<sub>2</sub> thermal desorption for 2 series of supported catalysts (see Table 3) are shown on Fig. 3 in the coordinates  $\ln v_0$  versus  $E_d$ .

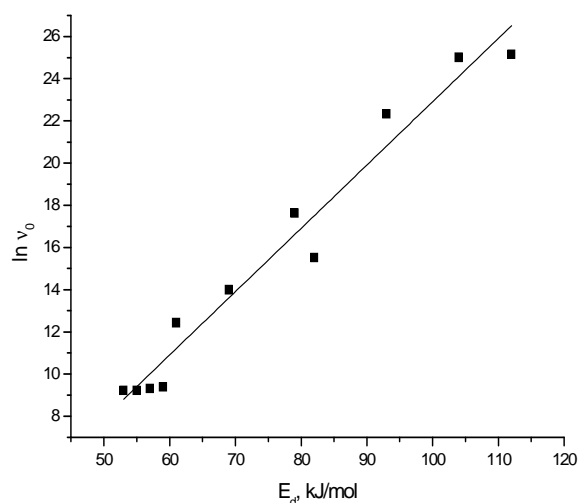
The slope of the compensation line equals to  $(3.00 \pm 0.19) \cdot 10^{-4} \text{ mol} \cdot \text{J}^{-1}$  is in agreement with slopes of above-mentioned theoretically probable lines and almost doesn't differ from that of compensation line obtained from the catalytic experiments.

**Table 3.** Experimental values of the kinetic parameters

Sample	Catalytic experiments data				CO <sub>2</sub> TPD profiles data		
	$t^{100}, ^\circ\text{C}$	$\ln k_0$	$E, \text{kJ} \cdot \text{mol}^{-1}$	$T_M, ^\circ\text{C}$	$v_0, \text{c}^{-1}$	$E_d, \text{kJ} \cdot \text{mol}^{-1}$	$\ln v_0$
CNT <sub>Fe</sub> /10	168	19.0	91	226	$1.0 \cdot 10^4$	53	9.2
CNT <sub>Fe</sub> /20	180	17.2	83	250	$2.5 \cdot 10^5$	61	12.4
CNT <sub>Fe</sub> /30	157	26.7	112	220	$5.5 \cdot 10^6$	82	15.5
CNT <sub>Fe</sub> /40	151	25.7	108	176	$1.2 \cdot 10^6$	69	14.0
CNT <sub>Fe</sub> /50	167	23.1	103	221	$1.2 \cdot 10^4$	59	9.4
CNT <sub>Ni</sub> /10	214	15.3	82	164	$1.1 \cdot 10^4$	57	9.3
CNT <sub>Ni</sub> /20	180	35.2	150	189	$7.3 \cdot 10^{10}$	104	25.0
CNT <sub>Ni</sub> /30	201	29.7	138	209	$5.0 \cdot 10^9$	93	22.3
CNT <sub>Ni</sub> /40	155	38.4	151	188	$8.4 \cdot 10^{10}$	112	25.2
CNT <sub>Ni</sub> /50	157	21.2	101	161	$4.5 \cdot 10^7$	79	17.6
CNT <sub>Ni</sub> /20+20	175	13.3	67	187	$1.0 \cdot 10^4$	55	9.2



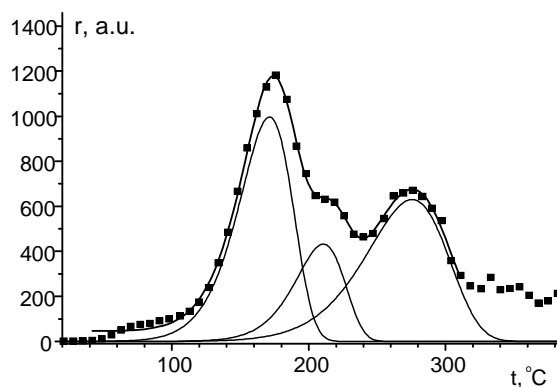
**Fig. 2.** Theoretically possible compensation lines calculated from Eq. 5, for 150°C (■), 200°C (●) and 250°C (▲)



**Fig. 3.** Compensation line for CO<sub>2</sub> desorption process from the surface of CNT-supported samples after catalysis

It can be seen from the given data set that both rate-limiting step (CO oxidation on the surface with the formation of adsorbed CO<sub>2</sub>) and desorption of CO<sub>2</sub> possess simultaneously high or low values of kinetic parameters. One can suppose that these are in respect to different forms of adsorbed CO<sub>2</sub> on the surface.

It is known from the literature data [24] that CO adsorption on oxides can lead to the formation of several different forms of adsorbed species. The next forms are marginal by energy: the surface carbonate form (possessing low values of the activation parameters of desorption) and the surface formate form (possessing high values of mentioned parameters). Both the formation and the decomposition of surface carbonate have low enthalpy and entropy of activation. The formation of the surface formate must possess high activation entropy due to necessary structural rearrangement with hydrogen atom migration and can proceed only if surface –OH-group is available. It can be supposed that surface formates are formed on the surface of copper hydroxonitrate Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>. The decomposition of formate with simultaneous CO<sub>2</sub> desorption also has high activation entropy (due to atomic hydrogen formation) and high activation enthalpy (C–H bond is broken in the process of desorption in addition to surface bond).



**Fig. 4.** TPD MS spectrum of CO<sub>2</sub> from the surface of CuO after catalysis. 3 forms of CO<sub>2</sub> desorption are shown

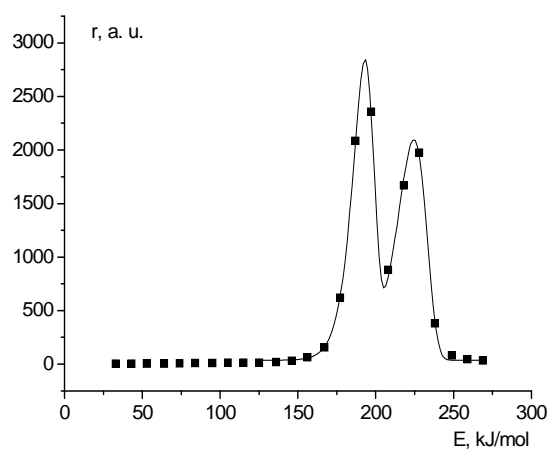
**Table 4.** Kinetic parameters of CO<sub>2</sub> desorption from the surface of CuO

Peak	$T_M, ^\circ\text{C}$	$E, \text{kJ}\cdot\text{mol}^{-1}$	$\nu_0, \text{s}^{-1}$
1	171	81	$3.8\cdot 10^7$
2	211	105	$2.5\cdot 10^9$
3	276	80	$3.4\cdot 10^5$

Fig. 4 and Fig. 5 demonstrate the TPD profiles of CO<sub>2</sub> from the surface of CuO after catalysis and of CO<sub>2</sub> formed in the decomposition of copper formate Cu(HCOO)<sub>2</sub> under the conditions of TPD experiment, respectively. TPD profile from CuO surface can be split to 3 desorption forms that are characterized by low values of desorption kinetic parameters and this corresponds to the decomposition of surface carbonates (Table 4). 2 forms of CO<sub>2</sub> desorption are observed on the TPD profile of Cu(HCOO)<sub>2</sub> and are characterized by high values of the kinetic parameters (Table 5). Indeed, carbonates and formates decomposition processes are characterized by significantly different parameter values.

**Table 5.** Kinetic parameters of CO<sub>2</sub> desorption for Cu(HCOO)<sub>2</sub>

Peak	$T_M, ^\circ\text{C}$	$E, \text{kJ}\cdot\text{mol}^{-1}$	$\nu_0, \text{s}^{-1}$
1	193	269	$7\cdot 10^{28}$
2	225	217	$2\cdot 10^{21}$



**Fig. 5.** TPD MS spectrum of CO<sub>2</sub> for the sample of Cu(HCOO)<sub>2</sub>

Thereby, the experimental data prove that the reaction product (CO<sub>2</sub>) can be adsorbed in different forms on the surface of catalysts of the studied series. Both CO oxidation reaction and CO<sub>2</sub> desorption occur in the narrow temperature interval but the kinetic parameters for both processes can differ significantly for different forms of adsorbed CO<sub>2</sub>. As a result, the integral kinetic parameters, determined for the whole sample, can take different intermediate values if different samples possess different ratios of quantities of

these forms on the surface. And because activation enthalpies and entropies are simultaneously increased or decreased due to change of adsorbed form (e.g., from carbonate to formate), the enthalpy-entropy relation is held for all series of the samples. The latter fact leads to the compensation relation.

As follows from the experimental results, active catalysts with low  $t^{100}$  demonstrate high values of pre-exponential factors and activation energies of CO oxidation reaction. Hence, for this type of catalysts it is possible to make the active sites with high activation energies of CO oxidation process, in particular, the sites on which the formation of surface formates is possible. This is in agreement with the data of the paper [11] where the conclusion was made that  $t^{100}$  is decreased if  $\text{Cu}_2(\text{OH})_3\text{NO}_3$  amount in the active mass of the catalyst is increased.

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Received 02.07.2010, accepted 17.08.2010

### Компенсаційний ефект на Cu-Co-Fe оксидних каталізаторах окиснення CO

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Показано наявність компенсаційного ефекту на нанесених та масивних Cu-Co-Fe оксидних каталізаторах реакції окиснення CO. На основі даних про стан поверхні, одержаних методом термопрограмованої десорбції з мас-спектрометричним аналізом (ТПД МС), запропоновано пояснення компенсаційного ефекту.

### Компенсационный эффект на Cu-Co-Fe оксидных катализаторах окисления CO

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Показано наличие компенсационного эффекта на нанесенных и массивных Cu-Co-Fe оксидных катализаторах реакции окисления CO. На основании данных о состоянии поверхности, полученных методом термопрограммированной десорбции с масс-спектрометрическим анализом (ТПД МС), предложено объяснение компенсационного эффекта.