

Redox Transformations in the Surface Layer of Complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ Oxides ($\text{R} = \text{Nd, Ho, Y}$) and Their Catalytic Properties in CO Oxidation

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Abstract—Initial stages of redox transformations in the surface layers of complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides ($\text{R} = \text{Nd, Ho, Y}$) in the course of their interaction with CO and O_2 are studied under non-steady-state conditions by a pulse microcatalytic method. It is shown that the interaction of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases ($\text{R} = \text{Y, Ho, Nd}$) with CO results in the removal of a weakly bound oxygen and in the formation of a surface layer of $\text{RBa}_2\text{Cu}_3\text{O}_y$ reduction products. It is found that $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides retain their ability to be oxidized after reductive treatment. Oxygen from the bulk phases of multicomponent $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides can take part in the catalytic oxidation of CO.

INTRODUCTION

Development of new heterogeneous catalysts for the selective oxidation of different organic compounds is one of the important problems in redox catalysis.

In this respect, multicomponent $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides, where R is a rare-earth element, are of interest. They are characterized by the high mobility of oxygen in a crystalline structure; anionic nonstoichiometry, which can change substantially while retaining a sample as a single-phase system [1]; and low activation energies of oxygen diffusion [2, 3]. These factors create conditions for controlling the concentration of “active” oxygen on the catalyst surface, and thus influencing selectivity. Information on possible transformations of the laminated cuprate surface exposed to a reaction medium under real conditions of a heterogeneous catalytic reaction is also of great importance for the development of new efficient catalysts based on complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides.

The goal of the present work is to elucidate a possible participation of bulk oxygen in $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Nd, Ho, Y}$) oxides in the catalytic oxidation of CO and to study initial stages of redox transformations in the surface layer of these compounds during their interaction with CO and O_2 under non-steady-state conditions.

EXPERIMENTAL

$\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Nd, Ho, Y}$) samples were synthesized by a high-temperature solid-phase reaction using the procedure described in [4]. The presence of a single phase in resulting oxides was monitored by XRD using an RD7 diffractometer with CuK_α radiation. The oxy-

gen nonstoichiometry was determined by iodometric titration [5].

The specific surface areas (S_{sp}) of multicomponent oxide powders were measured by the BET method (low-temperature nitrogen adsorption) using an ASAP-2000 instrument (Micromeritics, USA). Before measurements, the samples were degassed in a vacuum at 573 K to a residual pressure of 1.0×10^{-3} torr. The values of S_{sp} for $\text{YBa}_2\text{Cu}_3\text{O}_y$, $\text{NdBa}_2\text{Cu}_3\text{O}_y$, and $\text{HoBa}_2\text{Cu}_3\text{O}_y$ phases were 0.82 ± 0.01 , 0.41 ± 0.01 , and $0.84 \pm 0.01 \text{ m}^2/\text{g}$, respectively.

Redox transformations of the surface of $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides during their interaction with carbon monoxide and oxygen, as well as the catalytic properties of these compounds in CO oxidation, were studied under non-steady-state conditions by the pulse microcatalytic method.

Figure 1 presents the schematic diagram of a setup for kinetic experiments. Reagents were supplied in a pulse mode using a six-way cock connected with a 1-ml chromatographic loop. When the cock was turned, a pulse of the reaction mixture transferred into the system with the carrier gas (helium, $75 \text{ cm}^3/\text{min}$). Before the next pulse, the chromatographic loop was purged with the reaction mixture for 1 min.

A portion (0.2–0.3 g) of the test sample was placed on the glass filter of a quartz tube-in-tube reactor. The gas containing a portion of the reaction mixture entered the internal tube of the reactor from the system and reacted with the sample. Before the experiments, the samples were isothermally treated in a helium flow at 773 K for 4 h to remove water and CO_2 molecules adsorbed on their surfaces.

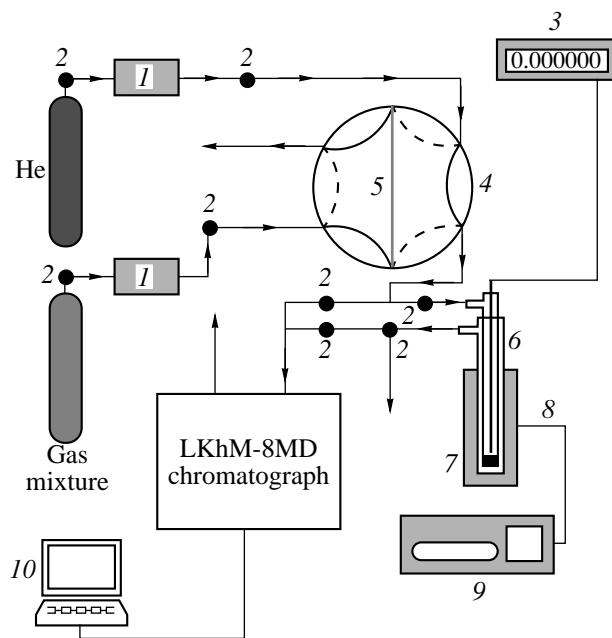


Fig. 1. Schematic diagram of the setup for pulse microcatalytic studies: (1) drying columns; (2) fine-adjustment valves; (3) digital voltmeter; (4) six-way cock; (5) calibrated chromatographic loop; (6) catalytic reactor; (7) oven; (8) thermocouple; (9) temperature controller; (10) computer.

Kinetic experiments were carried out under isothermal conditions in the temperature range from 373 to 673 K at 50-K intervals. Temperature was controlled with a thermocouple arranged directly in a quartz capillary in the catalytic reactor. Temperature was maintained constant to within ± 1 K.

The reduction of a complex oxide surface was studied in the reaction mixture containing 10 vol % of carbon monoxide in helium. In the studies of CO oxidation over $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides ($\text{R} = \text{Y, Ho, Nd}$), the reaction mixture containing 10 vol % of CO and 5 vol % of O_2 in helium was used.

At the system inlet, gas flows of reagents were passed through drying columns with silica gel.

The composition of the gas phase was monitored by chromatography using an LKhM-8MD chromatograph equipped with a thermal-conductivity detector. Analyses of the $\text{CO}-\text{CO}_2$ and $\text{O}_2-\text{CO}-\text{CO}_2$ mixtures lasted 2 and 5 min, respectively. The former mixture was analyzed using a column packed with Porapak Q at 35°C, and the latter mixture was analyzed using a column packed with SKT carbon at 85°C. Therefore, pulses of reagents were supplied every 3 min in the kinetic study of redox transformations of the complex oxide surface and every 6 min in the study of catalytic properties of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases ($\text{R} = \text{Y, Ho, Nd}$) under non-steady-state conditions.

Chromatographic analyses were automated an EKOKhROM program-and-instrument complex (Russia). The recording of chromatograms started simulta-

neously with the supply of a reagent pulse into the system and finished when all of the components left the column. The amounts of consumed (CO , O_2) and formed (CO_2) substances were determined for each pulse from chromatographic peak areas using calibration graphs. The rate of oxide surface reduction and that of catalytic CO oxidation were calculated by the formula [6]

$$w = \frac{V_i}{\tau S_{sp} m}, \quad (1)$$

where V_i is the volume of the transformed substance (cm^3); τ is the contact time of an oxide sample with a gaseous reagent pulse (s), defined as a ratio of the volume of reagent pulse V (cm^3) to the rate of a carrier gas flow U (cm^3/s): $\tau = \frac{V}{U}$; S_{sp} is the specific surface area of a sample (m^2/g); and m is the sample weight (g).

The error in the determination of the reaction rate w calculated assuming the errors in (a) chromatographic analysis, (b) maintaining the carrier gas flow at a constant rate, (c) temperature control of the reactor, (d) weighing the samples, and (e) measuring their specific surface areas was at most 10%.

RESULTS AND DISCUSSION

The formation of active sites and the development of a heterogeneous catalytic reaction are largely governed by processes occurring in the surface layer of a catalyst at the initial instant [6, 7]. Therefore, the study of initial stages of catalyst interaction with a reaction mixture is extremely important for understanding the mechanism of catalytic reactions and predicting catalyst properties.

To study transformations in the surface layer of rare-earth-element complex oxides with an $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Y, Ho, Nd}$) composition during their interaction with oxygen and carbon monoxide, we chose the pulse microcatalytic method [6, 7]. Advantages of this method are simplicity, high accuracy and sensitivity, feasibility of studies under real conditions of heterogeneous catalysis, and short times of analyses.

Redox Transformations in the Surface Layer of Complex Oxides $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Nd, Y, Ho}$)

In the experiments on the reduction of complex oxide systems, we took into account both a reversible change in the anionic nonstoichiometry y of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases from 6 to 7 and differences in the reactivity of oxygen atoms occupying nonequivalent positions in the crystal lattice. The following three non-equivalent crystallographic positions of oxygen can be distinguished in the $\text{RBa}_2\text{Cu}_3\text{O}_y$ structure: chain oxygen O(1) in the layers of (CuO_2V) , apical O(4) in the layers of (BaO) and planar O(2) and O(3) in the layers of (CuO_2) [8]. A change in the anionic nonstoichiome-

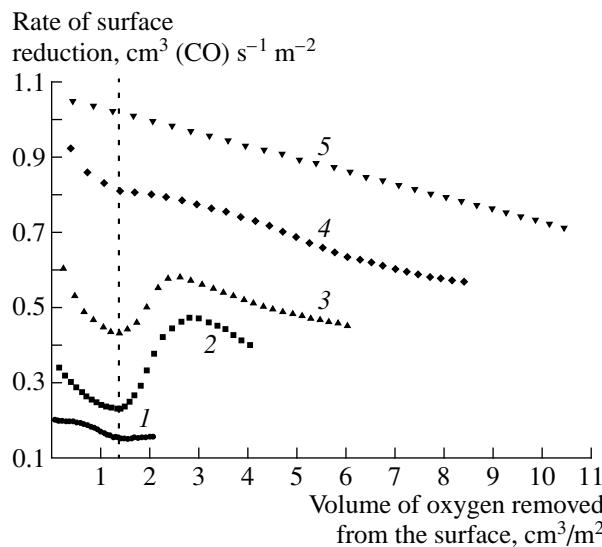


Fig. 2. Kinetic curves of the pulse reduction of the $\text{NdBa}_2\text{Cu}_3\text{O}_y$ surface (10 vol % CO) at (1) 473, (2) 523, (3) 573, (4) 623, and (5) 673 K.

try of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases was only due to the adsorption–desorption processes of chain oxygen atoms O(1). Oxygen in other positions (O(2), O(3), and O(4)) was activated, for example, in the processes of isotope exchange [8].

Figure 2 shows kinetic curves for the pulse reduction of the sample $\text{NdBa}_2\text{Cu}_3\text{O}_y$ surface, which is a representative of a multicomponent $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxide ($\text{R} = \text{Y, Ho, Nd}$), by carbon monoxide (10 vol % in helium). It follows from these curves that the kinetics of reduction was different at high (623–673 K) and low (473–573 K) temperatures.

At low temperatures, three portions of kinetic curves corresponding to different processes that occurred in the surface layer of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases can be distinguished (Fig. 3).

At the stage that corresponds to region I in Fig. 3, weakly bound oxygen was removed. Apparently, this was the oxygen that occupied the O(1) crystallographic positions in the $\text{RBa}_2\text{Cu}_3\text{O}_y$ crystalline structure. Each pulse of the reducing agent stripped a certain amount of oxygen off the complex oxide surface. Between the pulses, anionic vacancies formed in the surface layer were healed by bulk-phase oxygen in the course of bulk diffusion. As the concentration of weakly bound oxygen in $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases decreased, the rate of surface reduction monotonically lowered, and a highly defective, anion-deficient crystalline $\text{RBa}_2\text{Cu}_3\text{O}_y$ structure was formed. It is likely that the rate became minimal when oxygen atoms were completely removed from the O(1) positions in the crystalline structure of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases at $y = 6$. This concentration of oxygen corresponded to the low-oxygen boundary of the phase stability of complex oxides. The position of this boundary is denoted by a vertical dotted line in Fig. 2.

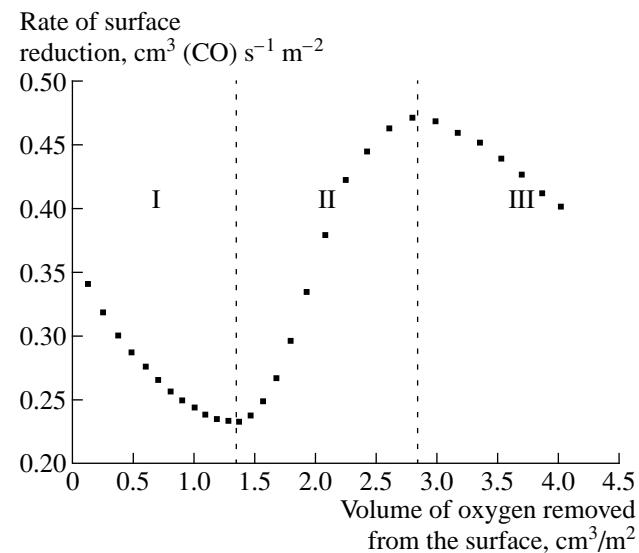


Fig. 3. Three portions of the kinetic curve corresponding to the occurrence of different processes in the surface layer of $\text{NdBa}_2\text{Cu}_3\text{O}_y$ oxide ($T = 523 \text{ K}$).

For the $\text{NdBa}_2\text{Cu}_3\text{O}_y$ phase the low-oxygen boundary shifted to higher values, because this oxide contained a larger amount of weakly bound oxygen compared with $\text{HoBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_y$ compounds, all other conditions being the same [4].

To test the assumption that weakly bound oxygen was removed at the initial stage of interaction between complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides and carbon monoxide, we compared initial portions of reduction kinetic curves for two $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples treated under different conditions before the experiment (Fig. 4). The first sample was treated in a standard way by exposure to a helium flow for 4 h at 773 K and cooled in helium to the temperature of the experiment (523 K). The oxygen concentration y in this sample was 6.04 as determined by iodometric titration. The second sample was treated in a similar way with the difference that 5 vol % O_2 was added to helium. This treatment increased the index of oxygen nonstoichiometry y of the complex oxide to 6.21. Assuming that only weakly bound oxygen O(1) of the crystalline structure was removed at the first stage of interaction between the $\text{YBa}_2\text{Cu}_3\text{O}_y$ phase and CO, the first and the second samples can theoretically lose 0.3 and 1.5 ml of molecular oxygen, respectively, provided the samples were equal in weight. Figure 4 shows that the boundaries of the first portion of reduction kinetic curves for the two $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples (they are denoted by vertical lines in Fig. 4) agree well with the calculated amounts of weakly bound oxygen. Thus, the rate of the surface reduction of complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides ($\text{R} = \text{Y, Ho, Nd}$) was minimal when these compounds reached the low-oxygen boundary of their phase stability, which corresponded to an oxygen concentration y of 6.

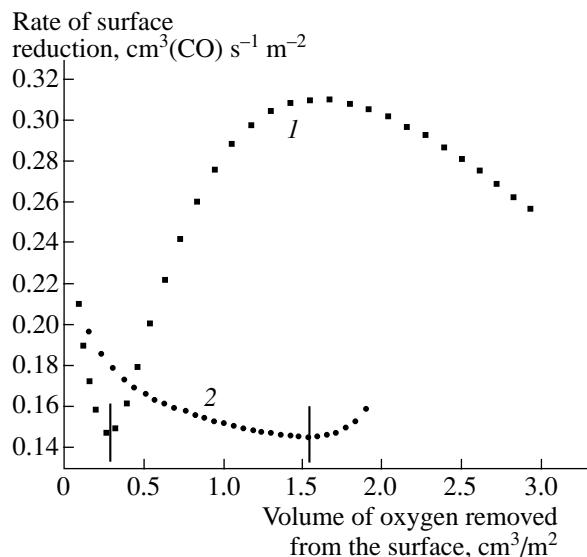


Fig. 4. Reduction of $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples (10 vol % CO) containing different amounts of weakly bound oxygen at 523 K: (1) sample preliminarily exposed to He and (2) sample preliminarily exposed to He + 5% O_2 .

Comparison of the absolute rates of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phase reduction in the initial portions of kinetic curves showed that the behavior of $\text{HoBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples was virtually identical, whereas the reduction of $\text{NdBa}_2\text{Cu}_3\text{O}_y$ occurred at rates twice as high as those for the $\text{HoBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples. This result is in good agreement with crystallochemical properties of complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides ($\text{R} = \text{Y, Ho, Nd}$). Because of a larger ionic radius R , other conditions being the same, $\text{NdBa}_2\text{Cu}_3\text{O}_y$ oxide contained a larger amount of weakly bound oxygen, and the processes of bulk diffusion in it occurred much faster [3, 4]. This resulted in an increase in the oxygen concentration in the surface layer and explained the higher rates of the heterogeneous reaction between this oxide and CO.

The second portion of the kinetic curve (region II in Fig. 3) corresponds to the phase degradation of multicomponent oxides. The rate of surface reduction drastically increased. This was caused by the localization of the reaction at the solid reagent–solid product interface and by the enhanced reactivity of the solid reagent at this interface. Rozovskii [7] comprehensively analyzed similar phenomena. Taking into account the complexity of the systems, one might expect simultaneous formation of several solid products in the reaction.

Noted that X-ray diffraction analysis of $\text{RBa}_2\text{Cu}_3\text{O}_y$ samples carried out after their exposure to the reductive atmosphere of CO has not revealed any contaminant phases. Phase degradation probably occurs only on the sample surface layer but not in the bulk phase of laminated cuprates. According to the XRD data, the dispersion of complex oxides after their interaction with CO

also remained unchanged. However, ESR studies showed that the magnetic properties of complex oxides changed significantly after reductive treatment. Isolated paramagnetic Cu^{2+} ions, $\text{Cu}^{2+}\text{–Cu}^{2+}$ dimers in a diamagnetic matrix, and a concentrated magnetic phase were formed [9].

A decrease in the rate of interaction between $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases and CO observed for the third portion of the kinetic curve (region III in Fig. 3) was due to two factors: (1) a decrease in the interface area of solid phases caused by the formation of a layer of reduction products at the sample surface [6] and (2) hindered diffusion of oxygen and CO through a layer of products.

Figure 5 presents kinetic curves plotted in $\ln w(\text{CO}) - 10^3/T$ Arrhenius coordinates. These curves exhibit all three stages of $\text{NdBa}_2\text{Cu}_3\text{O}_y$ phase reduction. Low activation energies indicate that the processes occurring in the system were limited by the diffusion of reagents (CO, O_2) to the boundary of heterophase interaction during the whole experiment.

The reactivity of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases toward CO at 623–673 K was so high that the surface layer of the solid-phase reaction products was formed already when the first pulse of CO reacted with a test sample. Therefore, portions I and II of the kinetic curve (see Fig. 3) that correspond to the removal of weakly bound oxygen and an increase in the reaction rate during the formation of the solid-phase interface cannot be observed. With every next pulse, the rate of $\text{RBa}_2\text{Cu}_3\text{O}_y$ reduction at 623–673 K decreased either because of the contraction of the solid-phase interface as the reaction proceeded to the center of single crystallites or because of the growing internal–diffusion retardation caused by the transport of reagents (CO, oxygen of solids) through the surface layer of reduction products.

In experiments on the reduction of multicomponent oxides, we simultaneously detected a change in the concentrations of all components of the gas pulse (CO and CO_2) before and after its interaction with a sample. It was found that, in the temperature range under study (473–673 K), the amount of carbon monoxide consumed from the gas mixture was equivalent to the amount of CO_2 formed. This fact pointed to the absence of the marked chemisorption of gas-phase components (CO and CO_2) on the surface of $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxides under the experimental conditions. At $T < 463\text{--}473$ K, $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases ($\text{R} = \text{Y, Ho, Nd}$) were not reduced by carbon monoxide (the chromatographic analysis of the reagent pulse after its interaction with a sample did not detect CO_2). At temperatures lower than 463–473 K, CO adsorption was not detected either, because the concentration of CO in the pulse after its contact with a solid surface coincided with the initial CO concentration to within the experimental error.

Note that the surface layer resulting from the reductive treatment of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases ($\text{R} = \text{Y, Ho, Nd}$) with carbon monoxide virtually had no effect on the subsequent reoxidation of multicomponent oxides.

This is very important for the use of these compounds as sources of activated oxygen in heterogeneous catalytic processes. Thus, Fig. 6 presents kinetic curves (5 vol % O₂) for the oxidation of two YBa₂Cu₃O_y samples. The first sample (the upper curve) was preliminarily treated with CO in a pulse mode at 673 K. The second sample (the lower curve) was exposed to a helium flow for 4 h at the same temperature before oxidation. The data show that the rates of the pulse oxidation of these samples and the amounts of consumed oxygen agree very well.

The absence of the surface barrier in the reoxidation of reduced RBa₂Cu₃O_y samples partially resolved the problem of degradation of these compounds under the conditions of heterogeneous catalytic reaction. The reactivity of RBa₂Cu₃O_y phases was extremely high [10]; however, their surfaces were contaminated with the reduction products of these compounds resulting from their interaction with the components of the reaction mixture, and the layer of the contaminant phases significantly retarded the further degradation of the complex oxide phase. Probably, the degradation of RBa₂Cu₃O_y catalysts may be avoided by the preliminary modification of their surface. It can be expected that the introduction of different modifiers into the surface layer would prevent the phase decay of RBa₂Cu₃O_y compounds, and the bulk phase of a complex oxide will be a source of activated oxygen.

Catalytic Properties of RBa₂Cu₃O_y Phases (R = Nd, Y, Ho) in the Oxidation of Carbon Monoxide

Figure 7 presents the kinetic curve plotted in the Arrhenius coordinates for CO oxidation over a HoBa₂Cu₃O_y catalyst. A similar pattern was observed for all the other test complex oxides: all curves plotted in the $\ln w(\text{CO}) - 10^3/T$ coordinates had an inflection point caused by the transition of the catalytic reaction from the kinetic to the diffusion-controlled regime. This inflection point corresponded with an accuracy of ± 20 K to the temperature at which the partial and complete heterophase exchange with the participation of bulk oxygen of laminated cuprates started on the surface of RBa₂Cu₃O_y oxides [4]. On the other hand, the temperature corresponding to the inflection point was independent of the total pressure in the experiments (1–2.5 atm), but it shifted to higher values ($\Delta T \approx 80$ K) with a decrease in the average size of

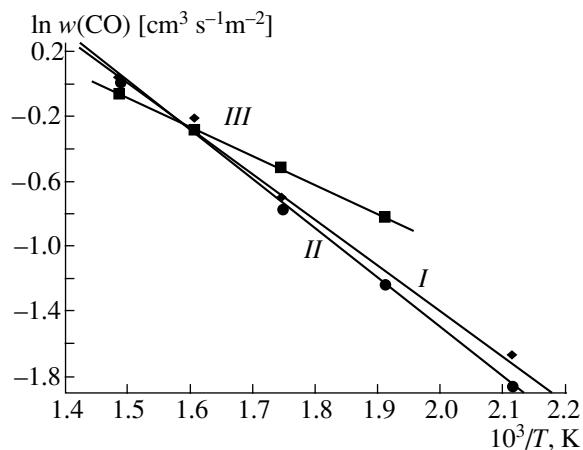


Fig. 5. Different portions of kinetic curves of NdBa₂Cu₃O_y reduction plotted in the $\ln w(\text{CO}) - 10^3/T$ coordinates (E_a , kJ/mol: (I) 23.4; (II) 25.5; (III) 14.8).

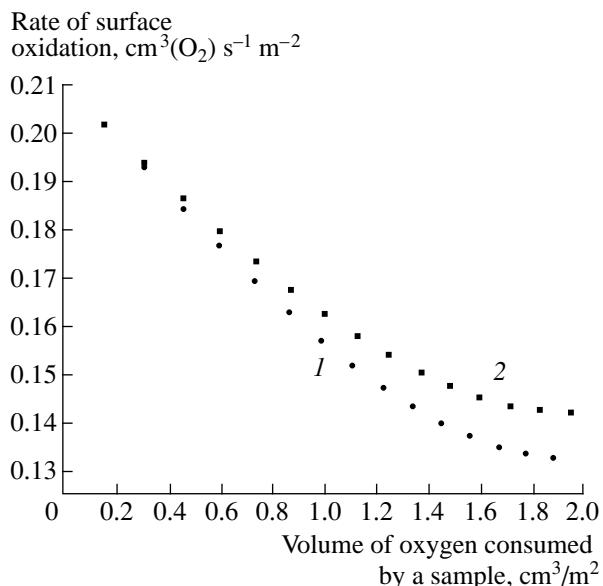


Fig. 6. Kinetic curves of the pulse oxidation of two samples of YBa₂Cu₃O_y complex oxide ((1) 673 K, He and (2) 673 K, CO).

granules from 50 to 25 μm . This led us to conclude that the oxidation of CO over complex oxide catalysts changed at a certain temperature to the internal diffusion mode that involved not only weakly bound oxygen

Activation energies of the catalytic CO oxidation under non-steady-state conditions on the surface of RBa₂Cu₃O_y (R = Nd, Y, Ho) oxide catalysts

Catalyst	Temperature of the reaction transition from kinetic to diffusion-controlled regime, K	E_a , kJ/mol	
		Kinetic regime	Diffusion regime
NdBa ₂ Cu ₃ O _y	532 \pm 5	68.4 \pm 4.5	22.8 \pm 1.1
HoBa ₂ Cu ₃ O _y	503 \pm 5	84.0 \pm 2.1	18.7 \pm 0.7
YBa ₂ Cu ₃ O _y	480 \pm 5	86.5 \pm 3.8	20.5 \pm 0.6

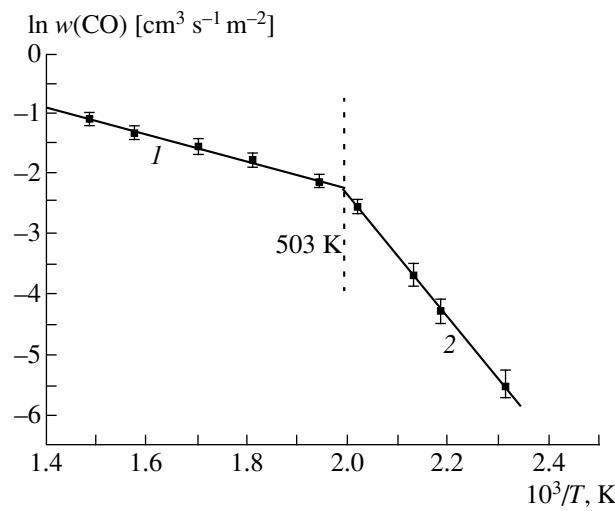


Fig. 7. Curves of the catalytic oxidation of CO on the surface of $\text{HoBa}_2\text{Cu}_3\text{O}_y$ phase plotted in $\ln w(\text{CO}) - 10^3/T$ coordinates (E_a , kJ/mol: (1) 18.7; (2) 84.0).

from the surface layer but also the weakly bound oxygen from the catalyst bulk phase. This result proves that the participation of bulk oxygen of multicomponent $\text{RBa}_2\text{Cu}_3\text{O}_y$ oxide systems in heterogeneous redox catalytic reactions is feasible.

The activation energies of catalytic CO oxidation on the surface of $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Nd}, \text{Y}, \text{Ho}$) are presented in the table. It follows from these data that $\text{NdBa}_2\text{Cu}_3\text{O}_y$ oxide is characterized by the lowest energy of oxygen binding to the catalyst surface, because E_a for this cuprate was minimal in kinetics-controlled CO oxidation.

As in the experiments on the reduction of the surface layer of multicomponent oxides, in the studies of catalytic properties of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases, we simultaneously detected a change in the concentrations of all components of the gas pulse (CO , O_2 , and CO_2) before and after its interaction with a sample. Neither CO nor CO_2 were noticeably chemisorbed on the surface of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases under the conditions of the catalytic reaction.

CONCLUSION

The pulse microcatalytic studies of complex $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Y}, \text{Ho}, \text{Nd}$) oxides performed in this work allowed us to obtain valuable information on possible transformations in the surface layer of these com-

pounds under non-steady-state conditions of catalytic processes. It was shown that the interaction of $\text{RBa}_2\text{Cu}_3\text{O}_y$ phases with CO resulted in the removal of weakly bound oxygen and in the formation of a defective structure. A surface layer of $\text{RBa}_2\text{Cu}_3\text{O}_y$ reduction products was formed that retarded the further degradation of the sample. It was found that, after the reductive treatment, $\text{RBa}_2\text{Cu}_3\text{O}_y$ ($\text{R} = \text{Nd}, \text{Ho}, \text{Y}$) oxides retained their ability to be reoxidized. Using CO oxidation as an example, we demonstrated that bulk oxygen in these complex oxides can take part in the heterogeneous redox catalytic process. This opens new possibilities for the use of catalysts based on laminated rare-earth cuprates as sources of activated oxygen for the selective oxidation of various organic compounds.

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