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Catalytic oxidation of CO on CuO$_x$ revisited: Impact of the surface state on the apparent kinetic parameters

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ABSTRACT

Analysis of kinetic features of the copper oxides reduction by CO pulses as related to mechanism of CO catalytic oxidation by oxygen combined with monitoring the state of the surface by an electrochemical technique using a solid electrolyte—Pyrex glass and high resolution TEM data on the defect structure of CuO allowed us to suggest a partially "flexible" model of CuO surface. This model, with a due regard for the data of FTIR spectroscopy of adsorbed CO test molecules, assigns the most active surface sites able to coordinate highly reactive CO and O forms to clusters of Cu$^+$ cations located at outlets of extended defects (dislocations, twins). Variation of the number, size and structure of these clusters under the reaction medium effect allows explaining the difference between quasi-steady and true steady states of copper oxides in catalytic CO oxidation reaction as well as the difference between kinetic parameters of reaction estimated at quasi-steady and constant states of the surface following Boreskov's approach. Kinetic features of the reaction agree with the Langmuir–Hinshelwood reaction mechanism operating for clustered defect centers of CuO.

1. Introduction

Investigation of the kinetics and mechanism of catalytic CO oxidation on transition metal oxides, including copper oxides, has relatively long history [1–4]. They still attract significant interest [5], particularly due to the problem of hydrogen purification from CO impurities [6–8]. In most recent reviews the important role of defect sites in the surface chemistry of both metals [9] and oxides [10–12] is discussed. Specific features of the reaction mechanism are also intimately related to the structure of active sites at the atomic-molecular level. For example, Red-Ox Mars-van Krevelen (MVK) mechanism usually involves the formation and filling of anionic oxygen vacancies on the oxide surface. Langmuir–Hinshelwood (L–H) mechanism assumes that low-coordinated adjacent metal atoms forming metal–metal bonds are present in the adsorption layer [8,9].

However, experiments carried out on single crystals of metal oxides are very limited and cannot "distinguish the chemistry of defect sites as their population and variety are deliberately manipulated" [11]. This is largely related to the existing limitations in the sensitivity of modern physical methods that do not allow for determining the structure and electronic state of elements at nanoscopic level, especially at the background of bulk oxides with the same chemical composition [11,12]. Additional factors limiting the application of kinetic methods in investigating the chemistry of surface defects are, in our opinion, relatively rough estimates of the reactivity of oxide single crystals because the small geometric surface area considerably constrains the capabilities in differentiating the surface properties of single crystals, varying the concentration of defects and applying non-steady-state methods, especially with realistic concentrations of reagents (well-known "pressure gap" problem).

For highly dispersed copper oxides, some data on comparison of the rates of catalytic oxidation reactions with the rates of separate steps of reaction mechanism were published [13–15]. For Cu$_2$O, the rate of complete oxidation of 1-hexene was compared to that of the carbonate–carboxylate complexes decomposition [13]. An "associative" mechanism of CO oxidation on CuO was suggested by Boreskov and Marshneva [14] on the basis of much lower rates of the catalyst reduction by CO as compared with the rate of catalytic reaction, in general agreement with the earlier conclusions of Roiter [15] and Fesenko et al. [16] as well as the later results of Rozovskii et al. [17]. However, the absence of any information on the real/defect structure of studied samples of CuO (not speaking about any control of its variation under the reaction media and its component effect) results in contradictory conclusions about the detailed mechanism of this reaction.

In the current study we aimed to elucidate specific features in the chemistry of defect sites on oxide surfaces using several types

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of bulk and SiO_2-supported copper oxide catalysts. The following approaches were used:

(A) Pulse techniques applied to finely dispersed oxides with high surface areas made it possible to introduce minimum perturbations to the state of the oxide surface while measuring the reaction kinetic parameters.
(B) The regularities of oxide reduction were first studied in detail in the pulse mode. This approach made it possible to analyze the dependence of catalytic activity on the phase composition and reduction degree of separate phases of Cu–O systems.
(C) The structures of extended defects in CuO were analyzed on the basis of high resolution transmission electron microscopic data and simplest models of active sites at their surface outlets.
(D) Specific features of the catalytic reaction kinetics in quasi-steady and true steady states of the copper oxide surface and the surface chemistry during pulse reduction were elucidated.
(E) The state of the surface was monitored by an electrochemical method using glass cation-conducting electrolyte [18]. The electrochemical methods of solid electrolyte potentiometry are rather informative in analyzing the surface properties of oxides under contact with reaction mixture, although cells based on oxide conducting electrolytes are used more widely [19].

2. Experimental

Several types of bulk copper oxides prepared by different methods were used in the study. “Nitrate” CuO was prepared by thermal decomposition of copper nitrates at 500 °C (specific surface area (SSA) = 0.40 m^2/g). “Wire” CuO (VEB Laborchemie Apolda) was prepared by oxidizing copper wire (SSA = 0.10 m^2/g). Cu_2O was synthesized from “nitrate” CuO by annealing in helium at 1000 °C (SSA = 0.15 m^2/g). Copper oxides with higher surface areas were used for non-steady-state experiments. “Hydroxide 1” CuO was prepared by precipitating from copper nitrate solution with NaOH followed by washing from sodium ions and calcination at 500 °C (SSA = 8.6 m^2/g). “Hydroxide 2” CuO was prepared by precipitating from copper nitrate solution with NaOH followed by washing from sodium ions and calcination at 500 °C under slightly different precipitation and drying conditions (SSA = 16.0 m^2/g). The concentration of impurities in the metal oxides did not exceed 0.1 wt.%. Supported CuO_x/SiO_2 (10 wt.% CuO) sample was prepared by impregnating A-300 aerosil (SSA = 300 m^2/g) with copper nitrate solution followed by calcination at 500 °C.

Kinetic studies were carried out in a pulse/flow catalytic installation in a glass reactor with a fluidized catalytic bed following the experimental procedures earlier described in detail [3,18,20]. Specific design of this kinetic installation equipped with several lines fed by gas streams of various compositions allowed us to supply into reactor the pulses of reagents with different compositions at a minimum (up to 1 s) time lag between pulses.

In the majority of experiments considered in this paper, the carbon imbalance was less than 10% rel. A bigger imbalance was observed in pulse experiments carried out at 25 °C (vide supra) due to readsorption of a part of CO_2 yielding carbonate–carboxylate surface complexes.

At temperatures exceeding 140 °C, continuous monitoring of the surface state of bulk oxides was carried out using an electrochemical method [3,18,21]. A thin wall of the working zone of specially designed Pyrex reactor served as a solid electrolyte, while a gold spiral contacting both the internal surface of the reactor wall and the powdered CuO catalyst (working electrode) served as catalytically/electrochemically non-active current collector. At the external reactor wall, Pt spiral covered with the Ag/AgO_x layer and purged by pure oxygen supplied into the shell surrounding the microreactor served as a reference electrode. From the measured values of the potential difference in this cell with a due regard for the asymmetry potential as described in details elsewhere [3], the oxide electrode potential E^* was estimated. This parameter is determined by the surface oxygen chemical potential (heat and entropy of adsorption) and Gibbs energy of oxide formation (Eq. (1)) [3,18,21]:

$$\begin{aligned} E* = {} & \frac{1}{2F}[\mu \mathrm{O}_{\mathrm{CuO}_{1-\delta}} - 1/2\mu^0\mathrm{O}_2] \\ & - \frac{1}{2F}[\Delta G^0_{T\,\mathrm{CuO}_{1-\delta}} - \Delta G^0_{T\,\text{“CuO”}}] + \Delta, \end{aligned} \tag{1}$$

where F is the Faraday number, μ is the chemical potential, $\Delta G^0_{T\,\mathrm{CuO}_{1-\delta}}$ and $\Delta G^0_{T\,\text{“CuO”}}$ are the standard thermodynamic potentials for the formation of a studied non-stoichiometric phase and a reference stoichiometric phase, respectively, and Δ is an increment characterizing the properties of copper cations incorporated into the surface layer of solid electrolyte and close to 0 for Cu–O system [3].

The rate of surface oxygen reduction by CO pulses was described by the kinetic equation $v = k\,p^{0.5}_{\mathrm{CO}}(1-\theta)L$, where k is the reaction rate constant ($s^{-1}\ Pa^{-0.5}$), p_{CO} is CO partial pressure (Pa), θ is the surface reduction degree, and L is specific concentration of oxygen atoms in the monolayer ($atoms/m^2$). The diffusion flow rate of oxygen atoms from the bulk of the catalyst to the surface layer was characterized using equation $v_d = k_d\theta L$, where k_d is a constant (s^{-1}) [20].

A mathematical model of reactor with a fluidized catalyst bed was constructed assuming that the reaction takes place under ideal mixing conditions and reaction mixture follows the ideal gas law. Pressure and temperature in the reactor were assumed to be constant. Then, the mathematical model taking into account the balance of oxygen atoms on the surface and CO molecules in the gas phase would look as follows:

$$\frac{d\theta}{dt} = k_1 y^{0.5}(1-\theta) - k_d\theta, \tag{2}$$

$$\frac{dy}{dt} = \frac{Q}{V_R}(1-y) - k_1 y^{0.5}(1-\theta)\frac{LGS}{N_A V_R C_{\mathrm{CO},0}}, \tag{3}$$

$$p_{\mathrm{CO}} = C_{\mathrm{CO}}RT, \tag{4}$$

$$t = 0 : \theta = 0, y = 0. \tag{5}$$

Here $y = C_{\mathrm{CO}}/C^0_{\mathrm{CO}} = p_{\mathrm{CO}}/p^0_{\mathrm{CO}}$ is the molar fraction of CO in a pulse in the reactor, $p^0_{\mathrm{CO}}, p_{\mathrm{CO}}$ are partial CO pressures at the reactor inlet and outlet, respectively, t is time, Q is the feed volume flow rate under experimental conditions (cm^3/s), V_R is the reactor volume (cm^3), $N_A = 6.023 \times 10^{23}$ is the Avogadro number (mol^{-1}), T is the reactor temperature (K), G is the catalyst weight, S is the catalyst specific surface area (m^2/g), and $k_1 = k\,p^{0.5}_{\mathrm{CO},0}$. This fractional CO order for CuO reduction was earlier revealed by Rozovskii and co-workers [22].

System (1)–(4) was numerically integrated with double precision using an explicit forth order Runge-Kutt-Merson with automatic choice of the step length. The acceptable error varied in the range of 10^{-8}–10^{-10}. The experiments and corresponding calculation were carried out using the following parameters: $G = 0.5$ g; $S = 0.1\ m^2/g$; $V_R = 1.7\ cm^3$; $Q = 1.537\ (cm^3/s)$; $p^0_{\mathrm{CO}} = 100$ Pa and $p^0_{\mathrm{CO}} = 23$ Pa; $T = 458$ K. The value of coefficient $k_d = 0.014\ s^{-1}$ was estimated from the reduction rate values at the minimum point (Fig. 1b). The average reaction rate constant k_1 was estimated without using any algorithm. At $p^0_{\mathrm{CO}} = 100$ Pa, $k_1 = 0.155\ s^{-1}$; at $p^0_{\mathrm{CO}} = 23$ Pa, $k_1 = 0.074\ s^{-1}$.

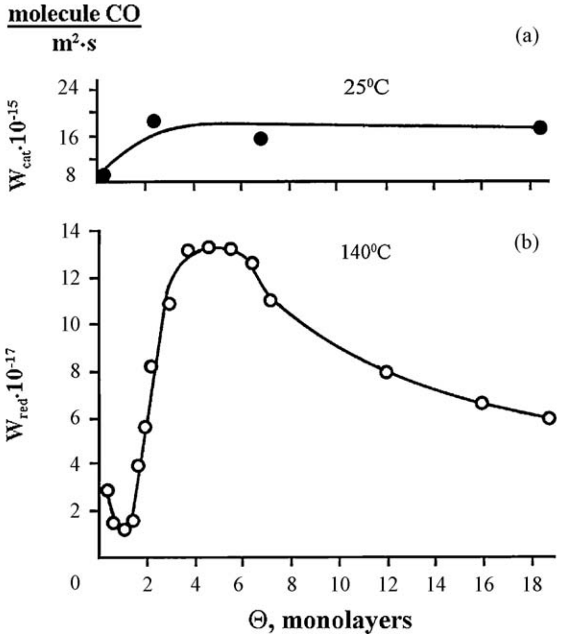

Fig. 1. Dependence of the catalytic reaction rate at 25 °C (a) and reduction rate at 140 °C (b) on effective reduction degree of "hydroxide 1" CuO (monolayers) at 140 °C in the pulse mode. Feed compositions: reduction—3 vol.% CO in He; reaction—1 vol.% CO + 1% O_2 in He.

3. Results and discussion

3.1. Specific features of copper oxide reduction under mild conditions: reduction kinetics and surface thermodynamics

In fundamental studies of the surface chemistry of oxides as related to catalysis of redox reactions, elucidation of their reduction kinetics as a catalytic reaction stage and/or stage of catalyst interaction with the reaction mixture is very important [1,17,22]. Fig. 1 presents a typical reduction profile of copper oxide powder by pulses of CO in He. Within the concepts the most consequently developed by Rozovskii et al. [17,20], at the initial, so-called "homogeneous" stage, the reaction rate decreases due to decrease of the surface oxygen concentration, oxygen atoms of CuO surface being uniform by reactivity. At this stage, only the initial CuO phase exists. Removal of oxygen atoms from the surface layer of CuO particles by CO pulse generates point defects—oxygen vacancies, while oxygen diffusion from the subsurface layers in the time interval between pulses replenishes in part the surface coverage by oxygen. At the minimum of the reduction curve (Fig. 1b), subsurface oxygen diffusion between pulses exactly compensates the amount of oxygen removed by CO pulse. When the oxygen capacity of the subsurface layers is more or less exhausted, the limits of thermodynamic stability of the reduced surface layers of CuO phase are exceeded, thus leading to nucleation of a new phase, Cu_2O. Due to reaction location at the interface between reduced CuO matrix and growing three-dimensional nuclei of Cu_2O phase, in the so-called "heterogeneous" region the reduction rate increases with the amount of removed oxygen (number of CO pulses). Although in this bi-phase range the size of Cu_2O nuclei is too small to be detected by diffraction methods, however, a constant value of the electrode potential E^* was indeed revealed as required for this monovariant system [21]. When the product nuclei merge into a continuous layer, the reduction rate reaches a maximum, since further thickening of the reduced product layer decreases the rate of oxygen diffusion through it [17,23].

Results of the detailed studies of CuO reduction are reported in Table 1. In the course of pulse reduction experiments (Fig. 2), the oxide electrode potential, which is determined only by the properties of oxide surface, first decreases under pulse action, then increases in the time interval between pulses. The decrease is due to oxygen removal by CO, whereas the increase is due to the surface oxygen recovery between the pulses by diffusion from the bulk of particles.

Mathematical description of the surface reduction in the "homogeneous" region was carried out assuming the surface oxygen to be uniform by reactivity (Table 1). It should be noted that the constant (k_1) (see Section 2) was normalized to the amount of reactive oxygen removed in the "homogeneous" region ($L = \theta_H \times 10^{19}$). The effective value of θ_H reached 3 monolayers (Table 1). A satisfactory match between the experimental and calculated data (Table 1) showed that the reduction process could be described by the uniform oxygen model in a wide range of experimental conditions and effective reduction degrees. Only when the amount of reactive oxygen was very high, nearly 3 monolayers, the discrepancy between the experiment and the calculation was significant (Table 1). It is clear that by definition the number of surface sites is restricted by the monolayer value. Hence, these results suggest that in fact, during pulse action, oxygen removed from the surface sites by CO is replenished via its migration from the subsurface layers with the rate greatly exceeding the rate of reduction, not speaking about the rate of diffusion estimated at the minimum of reduction curve. This is impossible within classic models of oxygen diffusion by jumps through vacancies created by reduction [24]. However, estimates obtained for polycrystalline oxides [25–28] show that diffusion coefficients along such extended defects as grain boundaries are many orders of magnitude higher than those within grains/domains even if point defects are present in the bulk. So, this result suggests that the high oxygen flux to the surface observed during reduction of CuO by CO pulses can be assigned to location of surface active sites in vicinity of extended defects providing a fast route of bulk oxygen supply to the surface.

Table 1
Kinetic parameters of "wire" CuO reduction by pulses 1 vol.% CO in He at 185 °C, $m = 0.5$ g.

Pretreatment	V_{pulse}, cm^3	Q, cm^3/s	p^0_{CO}, Pa	$y = p/p^0$	$W^0 \times 10^{-18}$[a], molec. CO m^2 s	Θ^0[b], mL		Range of CuO "homogeneity"	
						Exp.	Calc.	Θ_H[c], mL	N_H[c]
O_2	10.6	1.53	100	0.85	9.0	0.69	0.70	1.53	3
O_2	6.1	1.53	100	0.70	12.7	0.50	0.48	1.98	6
O_2	4.7	1.53	100	0.62	14.9	0.43	0.38	2.26	6
O_2	10.6	1.53	23	0.28	24.0	0.38	0.29	2.83	14
O_2	10.6	3.06	23	–	50	0.32	–	–	–
O_2, He	10.6	3.06	23	–	79	0.43	–	–	–

[a] Initial rate of reduction by [16].
[b] Reduction degree in the first pulse, monolayers.
[c] Number of pulses (N_H) and reduction degree (Θ_H) in the "homogeneous" region of CuO reduction.

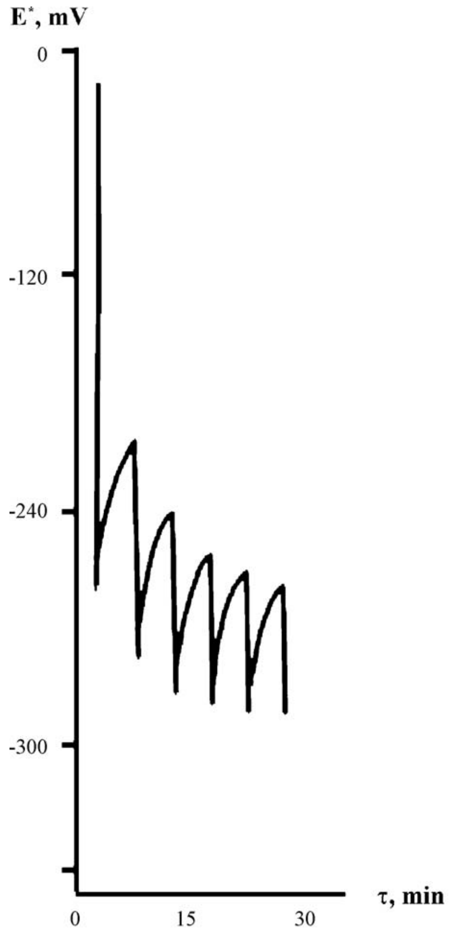

Fig. 2. Dependence of the electrode potential (E^*) of “wire” CuO powder on time in the helium flow with periodic pulses of reducing mixture 1 vol.% CO in He, pulse volume 10.6 cm^3, helium flow rate 60 cm^3/min.

Moreover, from adsorption studies, it is well known that oxygen on the surface of copper oxides is energetically non-uniform. For instance, isosteric heats of oxygen adsorption vary from 40 to 80 kJ/mol O_2 at reduction degree $\Theta \leq 1$–2% of the monolayer to 240 kJ/mol O_2 at $\Theta \sim$10% of monolayer [29,30]. Furthermore, a decline of E^* as CO is pulsed (Fig. 2) also suggests strong (nearly logarithmic) dependence of oxygen heat of adsorption (bonding strength) on the reduction degree, similar to [29,31].

This follows from Eq. (1) for “homogeneous” range of reduction, when nuclei of new Cu_2O phase are not formed and $\Delta G^0_{T\,\mathrm{CuO}_{1-\delta}} \approx \Delta G^0_{T\,\text{“CuO”}}$”:

$$E* = \frac{1}{2F}[\mu \mathrm{O}_{\mathrm{CuO}_{1-\delta}} - 1/2\mu^0 \mathrm{O}_2] = \frac{1}{4F}[-q_{\mathrm{O}_2} + T\,\Delta S_{\mathrm{O}_2}]. \qquad (6)$$

Here, $\Delta S_{O_2} \approx$ const is the entropy of oxygen adsorption (J/mol K), q_{O_2} is the heat of oxygen adsorption (kJ/mol K). According to [29,30], experimental dependence of the heat of oxygen adsorption on CuO on the reduction degree Θ q_{O_2} is close to the logarithmic one [29,30].

Hence, a strong variation of the E^* following insignificant variation of the oxygen coverage is mainly determined by variation of the oxygen bonding energy. Similar results were obtained for cobalt oxides as well as cobalt molybdates [31,32].

Even more surprising from the viewpoint of the surface oxygen state and its reactivity is the effect of He pretreatment on the initial rate of reduction (Table 1). Despite a significant decrease of E^* (an increase of the average energy of oxygen bonding with the surface), the reduction rate and surface reduction degree in the first pulse substantially increase after pretreatment in He. This discrepancy between the formal reduction kinetics of CuO and surface oxygen energetics suggests that the concentration of active sites where CO reacts with the surface oxygen is rather low.

Within the well-known approaches to description of kinetics of catalytic reactions, non-uniformity of the surface oxygen by energy is to be reflected in strong variation of the rate constant of the oxygen removal from the surface on its coverage or surface reduction degree. The simplest approach considered by Boreskov [1] suggests that “energy of active complex of ...the rate determining step... should change by some fraction of the change of the oxygen binding energy ...”:

$$\ln r \approx E = E_0 + \alpha q,$$

where r is the specific activity of the catalyst, E is the activation energy, q is the energy of the oxygen bonding with the oxide (heat of oxygen adsorption on the surface sites).

This approach, based upon consideration of the rate limiting stage of catalytic reaction—oxygen removal from the surface, is quite naturally valid for the analysis of reduction kinetics as well [33]. Certainly, if reduction of CuO in the “homogeneous” range proceeds with participation of non-uniform by bonding energy surface oxygen species (Table 1), any fitting of experimental data by model presented by Eqs. (2)–(5) would be impossible.

3.2. *Effect of mild reduction treatment on the low-temperature catalytic activity*

The effect of phase composition of Cu–O system on the observed kinetic parameters of CO catalytic oxidation has been extensively studied [2,4]. A typical drawback of such studies is the use of continuous flow mode for determining the kinetic parameters. Inevitable change of the surface composition under contact with reaction feed makes problematic the estimation of catalytic properties of a certain phase.

In our experiments, catalytic activity at different reduction states of Cu–O phases was estimated in the pulse mode and at low temperatures to minimize the effect of both reaction feed and bulk oxygen diffusion. Such experiments were carried out as follows. After several pulses of CO in He, the CuO sample was cooled in helium to 25 °C and its activity was tested by feeding CO + O_2 pulses. Then, the temperature was increased to 140 °C to continue reduction further followed by subsequent activity probing at 25 °C (Fig. 1). After transition to the “heterogeneous” region, the catalytic reaction rate increased approximately by a factor of two, in agreement with the earlier reported data [4]. However, subsequent growth of Cu_2O nuclei did not affect the catalytic activity. Hence, the activity is not proportional to the surface area of Cu_2O phase, and only its nuclei with minimal sizes provide a higher catalytic activity than the CuO phase.

Meanwhile, even a milder treatment in He at 310 °C (decreasing the surface oxygen concentration without phase transition into Cu_2O [20]) leads to a more significant (by more than an order of magnitude) increase in activity (Fig. 3). This suggests that not Cu_2O nuclei, but clusters of Cu^+ cations formed by mild reducing pretreatment of CuO [34] play the role of the most active sites. Fast decrease of the activity after pulsing the reaction mixture suggests that the reduced Cu^+ clusters are metastable, being readily oxidized by reaction mixture at room temperature. Similarly, oxidation of subsurface layers led to a decrease of the activity of copper metal [35,36]. In principle, a significant change of both the atomic structure and shape of copper oxide and supported metal particles due to the effect of reaction mixture is well known [19,37].

Hence, there is no simple relationship between the phase composition and specific activity in CO oxidation over Cu–O

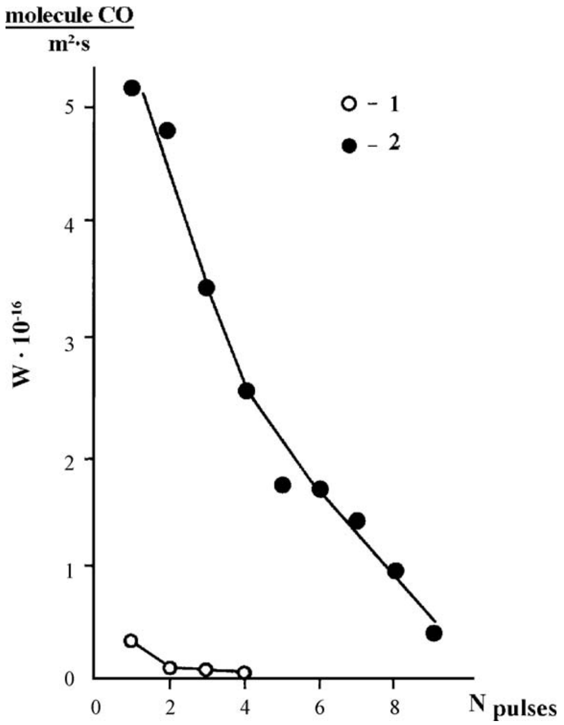

Fig. 3. Dependence of the catalytic reaction rate measured at 25 °C on the pulse number for 1% CO + 1% O_2 in He feed after different pretreatments at 310 °C: (1) treatment I (oxygen); (2) treatment II (O_2, then He). Pulse volume 6.1 cm^3, helium flow rate 60 cm^3/min, sample "hydroxide 1" CuO.

system. The reduced nature of CuO_x active sites is not determined by the presence of the Cu_2O or Cu^0 phase admixtures, but rather by the presence of smaller structures—reduced clusters.

3.3. Effect of deep and mild reduction on the apparent activation energy of CO catalytic oxidation over copper and copper oxides at a constant state of the surface

Activation energy of catalytic reaction is considered as an important kinetic parameter characterizing its mechanism. For L–H type mechanism of CO catalytic oxidation, activation energy is considered to be lower than for MVC mechanism due to more efficient rearrangements of chemical bonds within CO + O adsorption complex [4]. Application of this criterion requires the estimation of activation energies at a constant state of the catalyst surface probed by pulses of reaction feed at different temperatures [1], which in fact was not really followed earlier in any systematic manner. Here the term "constant state of the surface" primarily means the constant oxygen stoichiometry (reduction degree or the surface coverage by oxygen) along with the phase composition and real/defect structure. This can be provided by a fixed pretreatment procedure before each point of a series of kinetic experiments. In the flow of the reaction mixture, the surface coverage by adsorbed species could be constant versus time as well.

In our experiments, the catalytic activity of supported CuO_x/SiO_2 system was determined in the pulse mode, which minimized change of the surface state of copper oxides. The catalyst was preliminary reduced in hydrogen at 400 °C and purged with helium. The copper oxide deposition on silica decreased the probability of its sintering during reductive treatments. Before each experimental point, the catalyst was reduced in CO and purged by He at 300 °C. Then, the temperature was decreased to a required value, and 3 pulses of CO + O_2 feed were supplied. For a system close to Cu^0, E_a was ca. 12.6 kJ/mol (Fig. 4, curve 1). For the Cu^0 surface with a higher oxidation degree achieved after 3 pulses, E_a was ca. 30.4 kJ/mol (Fig. 4, curve 2). These results reasonably agree with the values reported by other researchers [4,37].

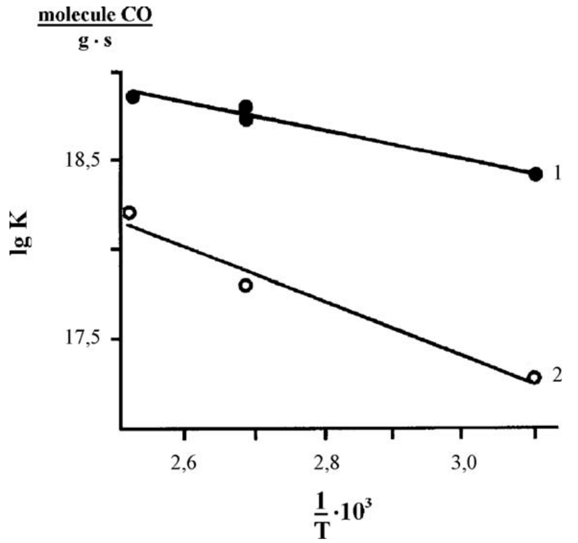

Fig. 4. Dependence of the reaction rate extrapolated to inlet feed composition on temperature for CuO_x/SiO_2 catalyst in Arrhenius coordinates after reductive treatment in hydrogen and CO for the first (1) and third (2) pulses of reaction mixture 1% CO + 1% O_2 in He. Pulse volume 6.1 cm^3, helium flow rate 60 cm^3/min. The experimental procedure is described in the text.

The effective activation energy can decrease not only when CuO is transformed into Cu^0 by severe reduction. Mild pretreatments of bulk CuO_x in He without phase transformations have a similar effect. The experiments were carried out as described in Fig. 5 caption. First, the catalytic activity appeared to be significantly lower for the steady state in the reaction mixture both in the flow-through and pulse modes than after the He pretreatment. Second, E_a determined at approximately constant state of the surface after He pretreatment appeared to be considerably lower (ca. 55 kJ/mol) than in the feed flow in both the flow-through and pulse modes (76–84 kJ/mol), and rather close to the activation energy observed for the partially oxidized metallic copper (vide supra).

A high activation energy for the CuO obtained in the flow regime can be interpreted taking into account the variation of concentrations of active sites on the surface with temperature. In the reaction mixture the total concentration of active sites is lower than after the high-temperature pretreatment in He, but higher than after treatment in O_2 due to reduction of the surface by CO. When the temperature increases, the surface reduction degree in the reaction mixture increases (without CuO → Cu_2O phase transition [38]) and hence increases the number of clustered Cu^+ centers leading to a higher effective E_a.

Also one can suppose that the adsorption layer composition, surface coverage and type of adsorbed intermediates change in the reaction mixture with the temperature increase, thus affecting apparent activation energy of catalytic reaction. Heats of CO adsorption on Cu^+ cations vary from 80 to 108 kJ/mol [38]. Therefore, for these values of adsorption heats, in the studied temperature range, the surface coverage with CO indeed can change. However, this factor will operate both in the flow and in the pulse regime (at a constant state of the surface), hence, it does not explain a high activation energy in the flow regime. Carbonate–carboxylate complexes that are bound stronger cannot decrease the rate of low-temperature CO oxidation by an order of magnitude [8,34]. Moreover, as reliably demonstrated by in situ FTIRS studies, they do not prevent the low-temperature CO oxidation through adsorbed carbonyl complexes [39]. In general, the changes of the surface coverage by adsorption

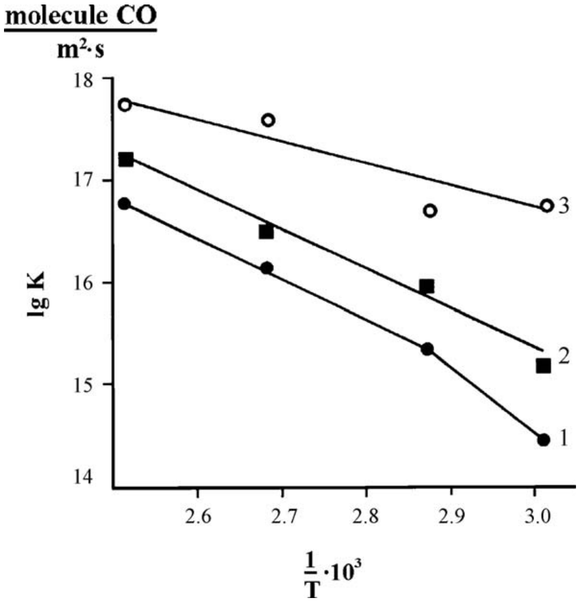

Fig. 5. Dependence of reaction rate constant on temperature for hydroxide CuO catalyst in Arrhenius coordinates measured in reaction mixture flow (1) and in pulse mode (2, 3). The reaction mixture composition 1% CO + 1% O_2 in He, feed and He flow rate 60 ml/min. Curve (2)—the reaction mixture flow over the catalyst was switched for helium followed by reaction mixture pulses. Curve (3)—experiments were carried out at a constant catalyst composition as follows. The CuO sample was pretreated in He flow at 310 °C. Then, the temperature was decreased to different values between 25 and 125 °C, and the catalytic activity was measured in the pulse mode (curve 3). After repeated pretreatment in He, catalytic activity was estimated at another temperature. Hence, the state of the oxide surface (its oxidation degree) remained approximately constant. The results were compared with the data obtained in the flow regime (curve 1). In addition, the catalytic activity was also measured in a pulse mode for the steady state of the surface under contact with the reaction mixture. In this case, at each temperature the reaction mixture flow over the sample was switched for He, and the activity was measured in a pulse mode (curve 2).

complexes can hardly account for the observed range of the catalytic activity variation when the concentration of potential adsorption sites is relatively low. It is more likely that the concentration or sizes of reduced copper ion clusters increase in the reaction mixture with the temperature growth as it was observed after a mild He treatment. This results in the increase of the effective active site concentration similar to the mild activation in helium. When the active site concentration is constant, the activation energies are low [37].

3.4. Model of partially flexible surface

As follows from the results presented in previous section, high-temperature reduction of CuO is accompanied not only by generation of point defects (oxygen vacancies), but also by nanoscopic rearrangement of the real/defect surface structure, which is to be taken into account in analysis of the forms of oxygen adsorption on the surface.

Semiempiric method of interacting bonds (IBM) earlier described in detail [29,30,40,41] was used in our case for such an analysis. In this method, an oxide is considered as comprised of interacting Me–Me and Me–O bonds. The energy of formation of a complex multiatomic system like copper oxide is represented as follows:

$$H_{\mathrm{at}} = \sum_{ik} \nu_{ik} E_{ik} = \sum_{i} [\varepsilon_i + \nu_i (2 - \nu_i) E_i] - \sum \sum_{i > k} \nu_i \nu_k \Delta_{ik},$$

where semi-empirical parameters ε_i and E_i characterize the strength of the ith bond, Δ_{ik} characterizes the interaction between ith and kth bonds, and the variable coefficients ν_i are determined from the maximum of atomization enthalpy H_{at}. This method allows one to estimate not only the bulk, but the surface oxide characteristics as well.

The reactivity of the transition metal oxides surface in the low- and medium-temperature ranges is mostly determined by weakly bound oxygen forms [1]. To determine the relationship of these forms with the specific features of mild reduction of copper oxides and microstructures formed on the surface, we analyzed the dependence of adsorption energies ($q_{O_2} = RT^2(\partial \ln pO_2/\partial T)_\theta$ (here θ is the surface coverage by oxygen) on the surface reduction degree for three different surface models [42]. Each adsorption site was characterized by adsorption equilibrium constant K_i at certain temperature T: $V_i + 1/2O_2 = (O)_i$, adsorption energy q_{iO_2}, and fraction of the surface corresponding to these sites α_i. Along with the oxygen adsorption, the processes of the adsorption centers reconstruction were taken into account with a due regard for their equilibrium. The equilibrium between sites (when reconstruction is possible) is characterized by constants $R_i = R_i^0 \exp(-\Delta H_i/RT)$, where ΔH_i is the enthalpy of the regular center transformation into ith defect center.

Main features of the surface models are as follows:

(1) Classic "rigid" surface with discrete inhomogeneity. Sites of different types cannot be transformed into each other: $\alpha_1 = 0.03$ (fraction of sites able to retain weakly bound oxygen forms); $q_{1O_2} = 10\,\mathrm{kcal/mol}$; $q_{2O_2} = 50\,\mathrm{kcal/mol}$; $K_2/K_1 = 1000$. These parameters are close to those typical of CuO in the "homogeneous" region, some specific features of this model are considered in [29]. In this case, consumption of highly reactive weakly bound surface oxygen forms (Fig. 6, curves 1 and 1′) results in a reduction rate decrease proportional to its concentration.

(2) "Flexible" surface where the sites are in equilibrium. This is an analog of a monovariant system during the first order phase transition typical of the CuO → Cu_2O transformation when E^* is constant [21]. In the simplest case, such model assumes the existence of two types (regular and defective) of surface sites, which have considerably different oxygen bond strengths. A regular site can be transformed into defective one by abstracting the surface oxygen. This model is physically based on the fact that a regular surface cation can migrate into the subsurface interstitial position after abstraction of the surface oxygen atom to form a metal–metal bond with another cation in a regular position, thus forming a cluster: $q_{1O_2} = 10\,\mathrm{kcal/mol}$; $q_{2O_2} = 50\,\mathrm{kcal/mol}$; $R_2 = 0.05$; $\Delta H_2 = 10\,\mathrm{kcal/mol}$; $K_2/K_1 = 1000$; α_1 grows with reduction. For such a model, the rate of reduction proportional to the product $\alpha_1\theta$ will be nearly independent of the reduction degree (Fig. 6, curves 2 and 2′). This agrees with a rather weak dependence of the catalytic reaction rate on the reduction degree for bi-phase CuO–Cu_2O system in the course of first-order phase transition, some increase being observed only after appearance of Cu_2O nuclei (Fig. 1a).

(3) A more general model of "partially flexible" surface. There are two types of sites (β and γ) on the rigid part of the surface, which are in equilibrium only with sites 1, but are not transformed into each other. This model can correspond to two types of ideal oxide faces, each of them contacting with a defect site: $q_{1O_2} = 10\,\mathrm{kcal/mol}$; $Q_\beta = 20\,\mathrm{kcal/mol}$; $Q_\gamma = 50\,\mathrm{kcal/mol}$; $a_\beta = 0.1$; $R_2 = 0.3$; $\Delta H_2 = 10\,\mathrm{kcal/mol}$; $K_\gamma/K_1 = 1000$; $K_\gamma/K_\beta = 100$ (Fig. 6, curves 3 and 3′).

Formally, the "partially flexible" surface model accounts for a minor change of the surface coverage with the reactive oxygen form ($q_{1O_2} = 10\,\mathrm{kcal/mol}$) and, consequently, the reduction rate of most oxides when the average oxygen bonding energy on the

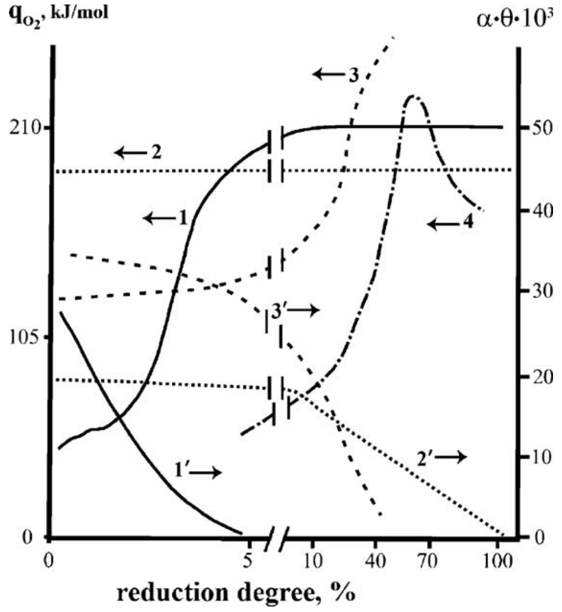

Fig. 6. Calculated dependences of average oxygen adsorption energy q_{O_2} (1, 2, 3, 4) and surface coverage with the reactive form (1′, 2′, 3′) on the average surface reduction degree according to models: 1—(1 and 1′), 2—(2 and 2′), 3—(3 and 3′) and (4).

surface as a whole changes significantly. At certain values of parameters not considered here for brevity [40,42], the model 3 makes it possible to obtain a maximum on the dependence of the average oxygen adsorption energy (Fig. 6, curve 4) and a minimum for the surface coverage with the reactive oxygen form. As a matter of fact, this model reflects activation of the surface with the formation of metastable systems at certain stages of oxygen abstraction from the oxide.

The main thermodynamic feature of metastable systems is that the chemical potential of the surface oxygen can increase when its concentration goes down, i.e. $(\partial\mu/\partial x)_{T,p} < 0$, where x is the component (oxygen) molar fraction. Such model can be proven by a weaker electrode potential dependence on the surface coverage with oxygen (θ_o) compared to the corresponding model of ideal solid solutions (ideal chemisorbed layer), i.e. positive deviation from the ideal model. Such deviations were indeed observed in our experiments on reduction of Cu–O solid solution [40]. In this way, the activation of the oxide surface after mild reductive treatment can be explained by the formation of metastable microstructures on the surface similar to the structures observed after mild oxidation of copper metal [43,44].

These results illustrate in a qualitative way the possibility of formation of different metastable nanostructures in copper oxides under different non-equilibrium processes. These nanostructures could substantially affect the characteristics of oxygen adsorbed on the surface of these oxides.

3.5. Real structure of surface defect sites and adsorbed forms of CO and oxygen

Structural sensitivity is observed in catalytic oxidation reactions on oxides if the most developed surface faces of the oxide particles are covered by strongly bound low-reactive oxygen forms. In this case, the active sites are localized at such places on the surface where defects changing coordination of cations prevent the formation of such forms [10]. However, the presence of over-equilibrium concentration of defects does not automatically lead to a high activity. This depends on the particular reaction mechanism and the local defects structure. In this section we shall analyze the possible active site structure and effect of reduction treatment on it taking a number of observed extended defects in the CuO structure as examples.

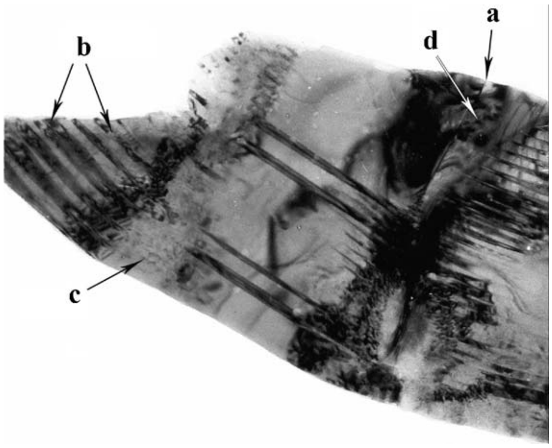

Fig. 7. TEM image of a CuO particle with defects: a—(1 0 0) twin; b—polysynthetic (0 0 1) twins; c—dislocation; d—microstrains.

A TEM image of "nitrate" CuO particle is shown in Fig. 7. One can see the following extended defects typical of copper oxide: polysynthetic twins in (0 0 1) plane, single twins in (1 0 0) plane, microstrains revealed as irregular shaped dark spots in the particle image and screw dislocations with Burgers vector along the $\langle 0\,1\,0\rangle$ direction. In more detail these defects were described earlier [45,46].

The simplest approach for analysis of atomic-scale factors leading to a high activity of defect centers, especially in the low- and medium-temperature regions, is related to their ability to retain weakly bound oxygen forms [1]. These forms account for the high activity either by themselves or by the formation of sites where CO molecules are activated when oxygen is removed. On ideal CuO faces, M_2O forms of adsorbed oxygen with adsorption energy ca. 240 kJ/mol predominate [29,30]. Less strongly bound MO forms of adsorbed oxygen with adsorption energy ca. 40 kJ/mol on the same regular sites can exist in amounts less then one percent of a monolayer. Steps formed at intersections of screw dislocations with the copper oxide surface can act as additional sites for oxygen stabilization on the oxidized surface. At places where (0 0 1) twins intersect with the surface (1 0 1) and (1 −1 −0) faces, another type of defect sites emerges where steric hindrances prevent the formation of M_2O adsorption forms [30].

As it was noted above, mild reduction of CuO surface takes place in the vicinity of outlets of extended defects. It significantly accelerates both reduction and catalytic reaction. Fig. 8 shows a model of a reduced (0 0 1) twin at its intersection with CuO (1 0 1) plane. Thermodynamic estimations carried out using the method of interacting bonds [45,46] showed that despite the fact that such nanostructure is obviously metastable, its formation energy (ca. 380 kJ/mol) is lower than the enthalpy required to abstract oxygen in the M_2O form from the surface to form an anionic vacancy (ca. 440 kJ/mol).

Such structure has several specific features (Fig. 8).

(A) A step is formed on the oxide surface.
(B) A new Cu–Cu bond compared to the ideal structure of an oxidized twin in the tenorite structure is formed when an oxygen atom is abstracted.
(C) Strongly bound oxygen forms like M_4O are formed at the basis of the step.

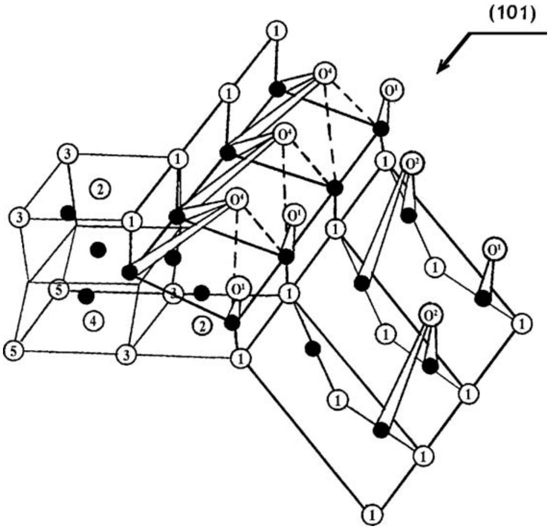

Fig. 8. Structure of the completely reduced (0 0 1) twin and its intersection with the (1 0 1) face of CuO [46]. O^1, O^2, O^4—adsorbed oxygen forms; O_1–O_5—lattice oxygen forms in different layers, numbers reflecting the distance from the (1 0 1) face.

(D) MO forms are formed on the step. Their reactivity is even higher than that of MO forms on ideal CuO faces due to steric hindrances caused by the four-coordinated oxygen form.

When all such MO forms are abstracted, the reduced nanoscale microstructures are CO adsorption sites with the charge close to Cu^{1+}. This corresponds to the CO adsorption sites observed after the vacuum treatment [38].

Thus, the presented active site model has all main potential chemical properties of the surface sites formed after mild reductive treatment.

3.6. Quasi-steady and true steady state activity of copper oxides

The problem of defect stability under reaction conditions is of fundamental importance. As was noted by Boreskov [1], a strong interaction between reaction media and catalyst should result in approximately identical state of the catalyst of a given chemical composition independent of its initial state (oxide stoichiometry, real/defect structure, etc.). Since all extended defects observed in CuO are metastable structures generated due to specificity of their genesis, their stability in reaction feed should be elucidated.

Fig. 9 presents the dependence of reaction constants on temperature in Arrhenius coordinates for CuO_x prepared by different methods. For samples 3–6 the curves were usually reproduced during the temperature rise and fall when the experiment was carried out in 1 day. The specific activity of the copper oxide samples differs strongly, though activation energy is very close. This implies that concentrations of identical active site on the surface are substantially different even for systems with the same phase composition.

After prolonged (up to 10^4 min or at least 10 days on-stream) contact with the reaction mixture at elevated temperatures, the activities of different CuO_x decrease and become identical (Fig. 9, curve 1). Moreover, the same level of steady-state activity was found for Cu_2O phase (Fig. 9, curve 2). Such changes in the activity are caused by annealing of extended defects due to accumulation of cationic and anionic vacancies in the tenorite lattice via the so-called "climb" mechanism and rearranging it into defect cuprite-type $Cu_{2-\gamma}O_{1+\delta}$ phase [3,47]. For stoichiometric cuprite Cu_2O, its oxidation by the reaction mixture rearranges its structure into that of defect disordered $Cu_{2-\gamma}O_{1+\delta}$ as well [3].

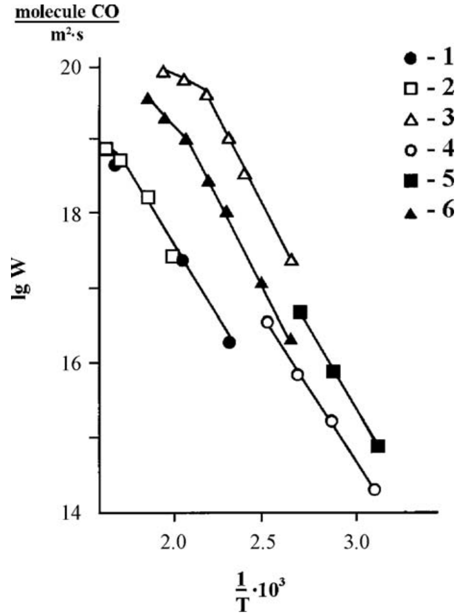

Fig. 9. Dependence of reaction rate (extrapolated to the inlet feed composition) on temperature for CuO_x samples prepared by different methods in Arrhenius coordinates estimated in a reaction mixture flow: (1,2) true steady state, (3–6) quasi-steady state; copper oxides sample: (1,6) "nitrate", (2) Cu_2O, (3) "wire", (4) "hydroxide 1", (5) "hydroxide 2".

Annealing of extended defects in CuO phase alters the oxide reducibility. Fig. 10 presents the curves for reduction of "wire" CuO. For this sample, in the steady state achieved after prolonged contact with CO + O_2 reaction medium, sample reactivity declines and reduction curve changes its shape, so that its "topochemical" part (where the rate increases with the pulse number) is lost. As was revealed by TEM and X-ray Small-Angle Scattering data [46,47], this is caused by annealing of extended defects, and, thus, disappearance of their surface outlets where the nuclei of the new phase are formed.

Hence, next distinct features of the quasi-steady state and true steady state of copper oxides for the reaction of catalytic oxidation

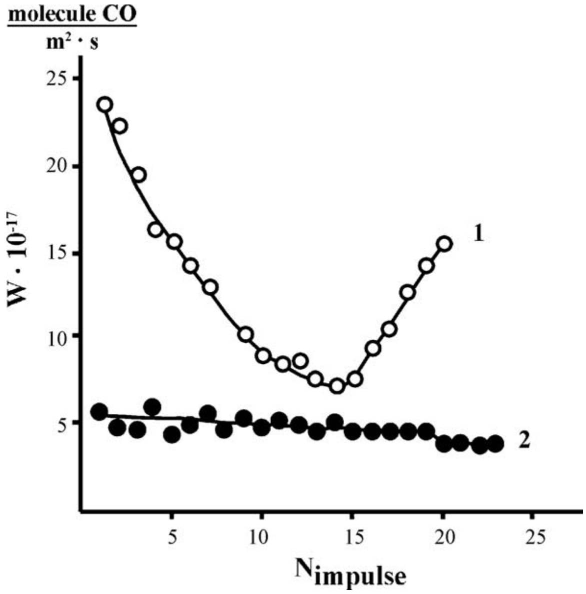

Fig. 10. Reduction rate versus reduction degree of "wire" CuO surface. Pulses of 0.23% CO in He, flow rate 60 cm^3/min, pulse volume 10.6 cm^3, experiment temperature 185 °C. Curve (1)—initial sample after oxygen treatment; curve (2)—sample after prolonged treatment in the reaction mixture.

of CO in feeds with a relatively small excess of oxygen (i.e. 1% CO + 1–5% O_2 in He or other inert gases) can be summarized:

(1) Quasi-steady state is characterized by the stationary degree of the surface oxygen stoichiometry (O/Cu ratio) and stationary surface coverage by different forms of adsorbed CO (carbonyls, carbonates, etc.), which is attained rather fast. However, the phase composition and real/defect structure of bulk and surface layers differ considerably, which provides different concentration of active sites.
(2) True steady state is the same for all phases in the Cu–O system and possesses the same structure based upon cuprite-like solid solution with enhanced concentration of point defects—cation and anion vacancies. It is thus characterized by close concentration of surface active sites and, hence, specific catalytic activity for all samples of copper oxides and metallic copper rearranged sooner or later into this true steady state, not speaking about the surface oxygen stoichiometry and the surface coverage by adsorbed complexes. Due to annealing of extended defects and, hence, the most active clustered sites situated at outlets of these defects, both the catalytic activity in CO oxidation and the rate of reduction by CO are much lower than for initial samples of CuO.

Hence, there are obvious differences between the quasi-steady state, which is traditionally determined under laboratory conditions, and the true steady state achieved in industrial reactors during extended runs [47]. This difference is caused by destruction of extended defects in the reaction mixture when point defects – cationic and anionic vacancies – are accumulated. The latter are commonly believed to account for the activity in catalytic reactions following the MVK mechanism [4,8]. A low activity of true steady state despite such high concentration of point defects agrees with a traditional point of view that L–H type mechanism of CO oxidation on metals is more efficient than that MKV-type mechanism on oxides due to more efficient rearrangement of bonds in the activated complex.

3.7. Mechanism of CO catalytic oxidation and real structure of the surface sites

As was shown above, in a quasi-steady state, when the concentration of clustered active sites is low and they are labile, minor changes in the gas phase composition or temperature can lead to significant changes in the properties of the active sites. At relatively high temperatures not only titration by individual components, but also the reaction mixture in general can alter the concentration of active sites. Therefore, it is of principle importance to maintain the same state of the surface to the maximum possible degree when performing experiments on determination of the reaction orders for individual components. Here the same state of the surface means similar surface coverage with possible adsorbed intermediates and approximately the same concentration of active sites [4]. Several experiments reported below illustrate this effect.

For instance, the CO order increased from 0.5 to 1 when the temperature was increased from 100 to 300 °C in a reaction mixture flow in a quasi-steady state (Fig. 11). This result suggests that the low- and medium-temperature CO oxidation indeed follows the L–H mechanism as in the case of platinum metals.

Fig. 12 presents the reaction rate dependences on the oxygen concentration in the reaction mixture at constant (pulse mode) or quasi-steady (flow mode) state of the surface. One can see that both dependences have maxima agreeing with the L–H mechanism where competition between CO and adsorbed oxygen in the adsorption layer takes place.

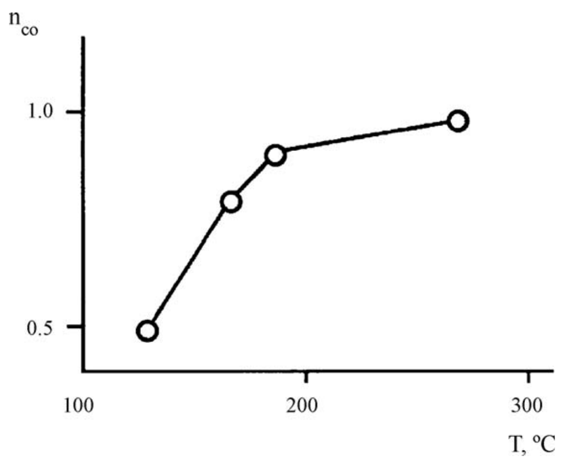

Fig. 11. Temperature dependence of CO reaction order over "nitrate" CuO for catalytic CO oxidation by oxygen in the quasi-steady state of the catalyst. The experiments were carried out by switching the flow over the CuO sample from the reaction mixture to the He stream. Feed composition in pulses: 1 vol.% O_2 + 0.3–1 vol.% CO in He, flow rate 60 cm^3/min.

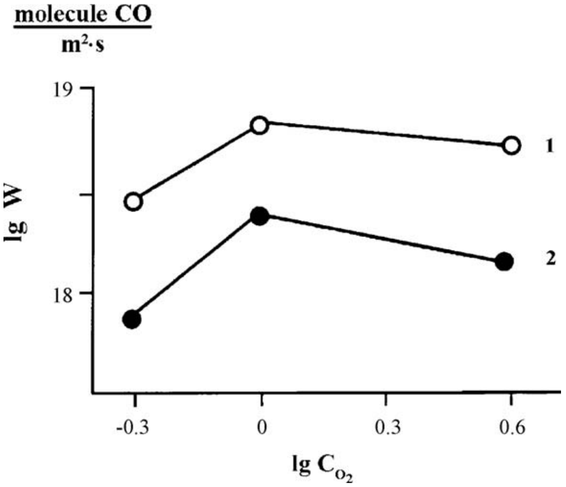

Fig. 12. Dependence of the catalytic CO oxidation rate on "nitrate" CuO on the oxygen concentration in the feed in pulse (1) and flow (2) modes. The experiment temperature 185 °C, CO concentration in the mixture with O_2 in He—1 vol.%.

As far as the reaction rate dependence on CO concentration is concerned, fractional order also agrees with the L–H type mechanism (vide supra). In the case of CuO, it is practically impossible to observe a decline of the reaction rate either in pulse or flow mode at the excess of CO content in the feed due to progressive reduction of the surface by CO. In the pulse mode, the expansion of cluster active sites under the action of reducing pulse will counteract the effect of a higher coverage of surface sites by CO, thus limiting the oxygen access. In the flow mode, progressive CuO surface reduction by the feed with the CO excess leading to phase transformation into Cu_2O, and, hence, continuous variation of the surface characteristics will make meaningless any comparisons of kinetic parameters.

4. Conclusion

The reported results lead us to a conclusion that the observed kinetics of reduction and catalytic CO oxidation over CuO at moderate temperatures is related to a relatively small number of active sites located at outlets of extended defects—paths of fast oxygen diffusion from the bulk. Mild reductive treatment results in additional activation of the CuO surface due to the increase of concentration of these active sites—clusters of Cu^+ ions. Specific features of the catalytic reaction kinetics observed when temperature in the reaction mixture or the concentration of individual components are varied are caused not only by the catalytic reaction mechanism itself, but also by changes in the concentration and properties of the active sites, which are very labile structures. These conclusions could be of a general significance for redox catalysis over transition metal oxides.

Hence, "one should keep in mind that bond breaking is generally facilitated by defects, so that overall kinetics of a catalytic reaction might be governed by the properties of these active sites rather than by those of the low-index crystal planes" [9].

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