Mechanism and kinetics of hydrogen oxidation on silver

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The kinetic study of the stationary oxidation of hydrogen on silver was carried out. The dependences of the reaction rate on the ratios of hydrogen and oxygen in the reaction mixture under a constant total pressure of 1000 Pa were obtained at 423, 448, and 473 K. The reaction seems to proceed *via* the intermediate formation of surface hydroxyls. A kinetic equation of the reaction that satisfactorily described the experimental data was derived.

Key words: silver, oxygen, kinetics of hydrogen oxidation.

Catalytic oxidation of hydrogen with oxygen on silver is interesting as a model redox catalytic reaction. At the same time, the reaction is practically significant for the solution of problems of power engineering that arise, in particular, in the development of fuel cells.

Based on the early studies[1—3] it was concluded that the reaction follows the mechanism including two consequent steps: chemisorption of oxygen and interaction of gaseous hydrogen with adsorbed oxygen. However, the subsequent works showed that the mechanism is more complicated and includes the intermediate formation of hydroxyls.[4,5]

The purpose of this work is to study the mechanism and kinetics of the catalytic oxidation of hydrogen. To describe the kinetic regularities, we used the results of previous works on separate studies of particular steps of the process of hydrogen oxidation.[4—6]

Experimental

The silver catalyst was prepared by the reduction of silver oxide with pure hydrogen. Silver oxide was precipitated from an aqueous solution of silver nitrate (99.9 wt.%, reagent grade, GOST 1277-75) with potassium hydroxide (special purity grade). After precipitation, silver oxide was thoroughly washed with distilled water and dried. The weight of the studied sample was 1.28 g, the silver granule size was 0.5—1.0 mm, and the specific surface area was 0.75 $m^2 g^{-1}$. The value of specific surface area was determined from oxygen adsorption at 473 K using the earlier[7] obtained isotherm of oxygen adsorption on a similar silver sample. The oxygen adsorption isotherm on silver was determined by both direct measurement of volumes of adsorbed oxygen and volumes of hydrogen consumed in the reaction with adsorbed oxygen. Therefore, the used isotherm of oxygen adsorption on silver describes the equilibrium between gaseous oxygen and oxygen adsorbed on the silver surface, which allowed a fairly exact determination of the silver surface using this isotherm. Oxygen dissolved in the near-surface layer of silver practically cannot be removed from the metal volume under the studied conditions and exerts no effect on the adsorption equilibrium of oxygen.[8]

The reaction was studied by the flow "differential" method[9] under the total atmospheric pressure of gaseous mixtures containing hydrogen, oxygen, and helium. Experiments were carried out at 423, 448, and 473 K under the constant pressure of the reaction mixture of hydrogen and oxygen: $P_{H_2} + P_{O_2} = 1000$ Pa (P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen, respectively, in the gaseous mixture). Reaction mixtures of required compositions were prepared using a system consisting of three reductors of gas dosage that provided a constant rate of the gaseous mixture passing through the reactor. In all experiments, the feeding rate of the gaseous mixture was 3 L h^{-1}.

The reactor was made of quartz as a cylinder with the bottom permeable for the gas (the bottom was made of superthin silica fiber). The catalyst was deposited on the bottom. One layer with the catalyst granules uniformly covering all the sectional area of the reactor was placed in the reactor. An optimum geometry of the reactor provided the uniform distribution of the reaction mixture flow over its cross section.

The reaction proceeded at very low changes in partial pressures of the starting substances: the conversion of the reaction mixture in experiments did not exceed 1%. A similar method of the reaction performance is named "differential." [9] At the same time, a necessary accuracy of determination of reaction rate was achieved by the freezing out and accumulation of water formed in the course of the reaction. Water was frozen out from the reaction mixture flow leaving the reactor in a spiral sampler cooled with liquid nitrogen. The sampler was made of a stainless steel capillary with an internal diameter of 2.5 mm. The length of the sampler directly cooled with liquid nitrogen was 50 cm. The rest part of the sampler was heated to a constant temperature (473 K) that was maintained inside the experimental setup and chromatograph. At first the sampler was cooled with liquid nitrogen, rapidly in 1 min the reaction mixture was introduced into the sampler; the duration of delivery of the reaction mixture

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ranged from 15 to 45 min, depending on the composition of the reaction mixture and, therefore, on the expected rate of accumulation of water formed. When the sampling was finished, the sampler was rapidly heated with silicone oil to 473 K, and one minute after the start of heating the sample was transferred to the chromatograph. The carrier gas (helium) and a mixture of gases were fed through the sampler and chromatograph in such a way that a continuous flow of helium through the chromatograph was ensured, and a flow of helium or the analyzed mixture could be introduced through the sampler at particular moments. Due to this, when the current sampling terminates, the sampler was filled with helium and the next sampling start to the moment of beginning of the next analysis.

Gaseous mixtures were analyzed on a Kristall-2000 chromatograph using a heat conductivity detector. Helium served as a carrier gas because it ensures a high sensitivity of the detector to the analyzed gases. Gases and mixtures of gases were subjected to the mandatory standard purification: oil was removed using Petryanov´s filter, carbon dioxide and water were removed using columns packed with zeolite and active carbon. Hydrogen and a mixture of hydrogen with helium were also purified from oxygen in a column with the nickel—chromium catalyst. The content of water vapor was determined using a column packed with the Porapak-T sorbent, and the amounts of oxygen and hydrogen were determined on columns packed with zeolites. The compositions of the initial mixtures were determined in control experiments. The water vapor pressure in the starting and final reaction mixtures was measured in the sampler with freezing out. The level of the water vapor content in the starting mixtures was lower than the detection limit.

Results and Discussion

The dependences of the reaction rate (rate of water formation) on the composition of the reaction mixture (expressed through the molar fraction of hydrogen in the reaction mixture with oxygen, X) are shown in Fig. 1.

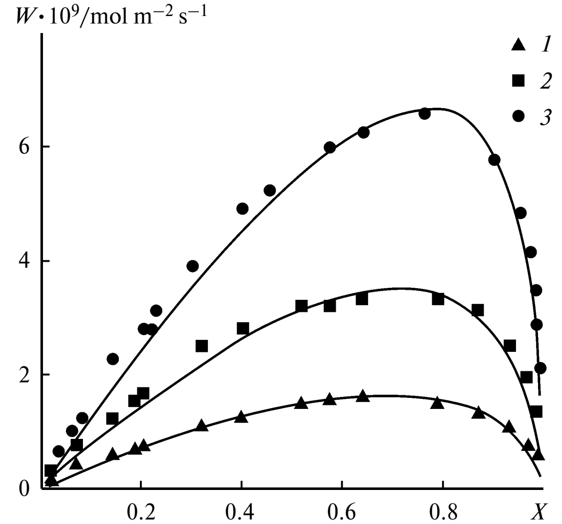

Fig. 1. Comparison of the experimental data at 423 (*1*), 448 (*2*), and 473 K (*3*) with the results of calculation (solid lines) using kinetic Eq. (9).

The dependences are described by curves with maxima near the stoichiometric composition. In the region of oxygen excess, at low molar fractions of hydrogen in the reaction mixture, the reaction follows the kinetic equation of the first order with respect to hydrogen

$$W = k_{H_2}P_{H_2}, \tag{1}$$

where W is the reaction rate, mol (of H_2 or H_2O) m^{-2} s^{-1}; k_{H_2} is the rate constant, mol m^{-2} s^{-1} Pa^{-1}; P_{H_2} is the partial pressure of hydrogen, Pa.

In the region of hydrogen excess, at molar fractions of hydrogen in the reaction mixture close to unity, the reaction follows the kinetic equation of the first order with respect to oxygen

$$W = k_{O_2}P_{O_2}, \tag{2}$$

where k_{O_2} is the rate constant, mol m^{-2} s^{-1} Pa^{-1}; P_{O_2} is the partial oxygen pressure, Pa.

Indices "H_2" and "O_2" in the designations of the reaction rate constants in Eqs (1) and (2) imply that the reaction rate constants in these equations are not true parameters of the specific steps but they only characterize the occurrence of the processes in the region of oxygen or hydrogen excess, where the first order of the reaction with respect to hydrogen or oxygen, respectively, is observed. These are experimental values, and their physical sense can be revealed only by studying the reaction mechanism.

The regions in which Eqs (1) and (2) are obeyed are different. The linear dependence of the reaction rate on the partial hydrogen pressure covers a considerable region of composition of the reaction mixture: from $X \approx 0.02$—0.03 to $X \approx 0.40$. At the same time, the linear dependence of the reaction rate on the partial oxygen pressure is valid only in a narrow range of molar fractions of oxygen ($Y = 1 - X$): depending on the temperature between $Y \approx 0.02$—0.07 and $Y \approx 0.01$—0.02. The experimental values of the kinetic parameters of the reaction are given in Table 1.

The results of separate studying of the reaction steps by isotope oxygen exchange,[10] adsorption kinetic methods using mass spectrometry,[4,6] and surface electron spectroscopy[11,12] suggest the scheme for the reaction mechanism (Scheme 1).

Scheme 1

$O_2 + 2\square = 2\,O_{ads}$ (slowly) (I)

$H_2 + 2\,O_{ads} = 2\,OH_{ads}$ (rapidly) (II)

$H_2 + OH_{ads} = H_2O + H_{ads}$ (slowly) (III)

$OH_{ads} + H_{ads} = H_2O + 2\square$ (rapidly) (IV)

In Scheme 1, O_{ads}, OH_{ads}, and H_{ads} are intermediate species adsorbed on the silver surface; □ are the equivalent

Table 1. Experimental and kinetic parameters of the reaction in an excess of oxygen (*A*) and hydrogen (*B*) and at the stoichiometric composition (*C*)

T/K	*A*		*B*		*C*	
	k_{H_2} /mol m^{-2} s^{-1} Pa^{-1}	*E* /kJ mol^{-1}	k_{O_2} /mol m^{-2} s^{-1} Pa^{-1}	*E* /kJ mol^{-1}	$W \cdot 10^9$ /mol m^{-2} s^{-1}	*E* /kJ mol^{-1}
423	$2.93 \cdot 10^{-12}$	47.9	$8.95 \cdot 10^{-12}$	84.5	1.62	46.5
448	$7.22 \cdot 10^{-12}$	47.9	$3.05 \cdot 10^{-11}$	84.5	3.32	46.5
473	$1.23 \cdot 10^{-11}$	47.9	$1.14 \cdot 10^{-10}$	84.5	6.56	46.5

sites of the surface capable of binding the intermediate species, and their number is equal to that of silver atoms on the Ag(111) plane of the silver single crystal. All steps are considered as elementary processes. Steps (I) and (III) are slower than steps (II) and (IV), which are fast and occur immediately after steps (I) and (III). Assumptions about the rates of the steps are based on the results of separate analysis the kinetics of these steps. The dissociative adsorption of oxygen on silver in the region of medium coverages of the surface occurs with an activation energy of ~60 kJ mol^{-1},[13] whereas the activation energy of step (II) is close to 20 kJ mol^{-1}. At ambient temperature, under the conditions of static experiment, step (II) is completed within ~1 min, whereas ~180 min are required for the overall step (V) including steps (III) and (IV) to occur.[4]

$$H_2 + 2\,OH_{ads} = 2\,H_2O + 2\square \tag{V}$$

Overall step (V) follows the kinetic equation of the first order with respect to hydroxyls,[4,6] *i.e.*, it follows the kinetic law of step (III) in Scheme 1. Therefore, step (III) is the rate-determining step in overall step (V) and, hence, occurs more slowly than fast step (IV).

It can be accepted that the mechanism of the fast steps is insignificant for the elucidation of kinetic regularities of the reaction, and their parameters are not included in the kinetic equation of the reaction.[14] The surface concentrations of intermediate particles O_{ads} and H_{ads}, formed in slow steps (I) and (III), are very low, since these particles immediately undergo further transformations and can be neglected. Thus, only slow steps (I) and (III) can be considered in the further kinetic analysis.

Taking into account the above statements, the rates of these steps are determined by the following equations:

$$w_{I} = k_{I}P_{O_2}(1 - \theta_{OH})^2, \tag{3}$$

$$w_{III} = k_{III}P_{H_2}\theta_{OH}. \tag{4}$$

The reaction rate (*W*) is as follows:

$$W = 2w_{III}, \tag{5}$$

since each elementary act of transformation in reaction (III) is accompanied by the elementary act of transformation in reaction (IV). The conditions of stationarity of the reaction can be expressed as follows:

$$m(d\theta_{OH}/dt) = 2w_{I} - 2w_{III} = 0, \tag{6}$$

where *m* is a value of the monolayer capacity, mol m^{-2}.

Inserting Eqs (3) and (4) into Eq. (6), we obtain for the rate of steps w_{I} and w_{III}

$$k_{I}P_{O_2}(1 - \theta_{OH})^2 = k_{III}P_{H_2}\theta_{OH}. \tag{7}$$

The following designations are used in Eqs (3)—(7): w_{I} and w_{III} are the rates of steps (I) and (III), mol m^{-2} s^{-1}; k_{I} and k_{III} are the rate constants of steps (I) and (III), mol m^{-2} s^{-1} Pa^{-1}; θ_{OH} is the coverage of the surface with hydroxyls.

The solution of square Eq. (7) gives the expression for the stationary coverage of the surface with hydroxyls and the kinetic equation of the reaction

$$\theta_{OH} = 1 + \frac{1}{2}\frac{k_{III}P_{H_2}}{k_{I}P_{O_2}}\left[1 - \sqrt{1 + 4k_{I}P_{O_2}/(k_{III}P_{H_2})}\right]; \tag{8}$$

$$W = 2k_{III}P_{H_2}\left\{1 + \frac{1}{2}\frac{k_{III}P_{H_2}}{k_{I}P_{O_2}}\left[1 - \sqrt{1 + 4k_{I}P_{O_2}/(k_{III}P_{H_2})}\right]\right\}. \tag{9}$$

The experimental kinetic data in Fig. 1 are compared with the curves calculated by the kinetic reaction Eq. (9). It is seen that the kinetic equation satisfactorily describes the experimental data. The divergences between the experimental dependences and results of calculations by Eq. (9) do not exceed 5—10% on the average, which corresponds to the usual inaccuracy of experimental studies. Perhaps, these divergences are caused by an inaccuracy of determination of the reaction rate constants. The comparison performed suggests the validity of the proposed mechanism and the kinetic model for the studied reaction.

The rate constants of slow steps (I) and (III) in reaction Scheme 1, which were used in the calculations of the reaction rate by kinetic Eq. (9), are listed in Table 2. The reaction rate constants were estimated using the inequalities

$$k_{I} = k_{O_2}, \tag{10}$$

$$k_{III} = 0.5k_{H_2}, \tag{11}$$

Table 2. Kinetic parameters of slow steps (I) and (III) that follow from an analysis of the reaction kinetics

T/K	Step (I)		Step (III)	
	k_{I} /mol m^{-2} s^{-1} Pa^{-1}	E_{I} /kJ mol^{-1}	$k_{\mathrm{III}} \cdot 10^{12}$ /mol m^{-2} s^{-1} Pa^{-1}	E_{III} /kJ mol^{-1}
423	$1.26 \cdot 10^{-11}$	68.7	2.2	38.6
448	$3.05 \cdot 10^{-11}$	68.7	4.5	38.6
473	$1.0 \cdot 10^{-10}$	68.7	7.0	38.6

where k_{O_2} and k_{H_2} are the experimental reaction rate constants in an excess of hydrogen and oxygen, respectively. The physical meaning of Eq. (11) is that each elementary act of reaction (III) is immediately accompanied by the elementary act of reaction (IV).

From the results of the studies it can be inferred that the adsorbed layer on the silver surface, under the conditions of the stationary reaction, consists predominantly of hydroxyls. Figure 2 shows the dependences of the coverage of the silver surface with hydroxyls on the molar fraction of hydrogen. These dependences were obtained using Eq. (8). These data are similar, although their mutual arrangement exhibits no regularity. Probably, this is a consequence of an inaccuracy of determination of the rate constants when using kinetic Eq. (9).

The experimental data are well described by a simple scheme of the mechanism including only two steps: the dissociative adsorption of oxygen and the interaction of adsorbed oxygen species with gaseous hydrogen. However, the mechanism disagrees with the results of separate studying of the reaction steps, which undoubtedly prove that the reaction involves surface hydroxyls as intermediates and the activated complex of the rate-determining step includes a hydrogen molecule and a hydroxyl (see step (III) of Scheme 1).[4,6]

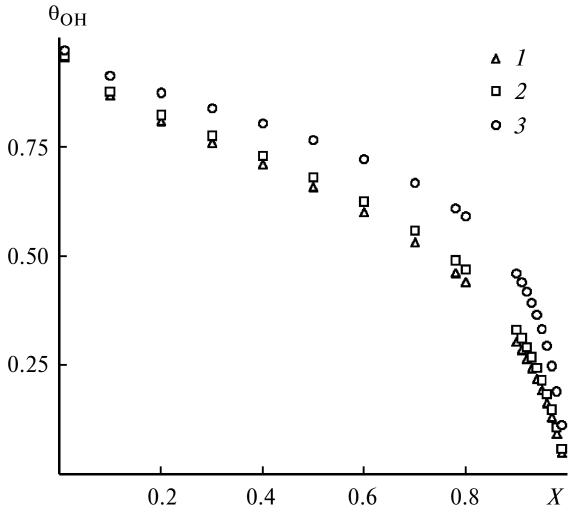

Fig. 2. Stationary coverage of the surface with hydroxyl groups (θ_{OH}) *vs* molar fraction of hydrogen (*X*) in the reaction mixture of hydrogen and oxygen calculated using Eq. (8) at 423 (*1*), 448 (*2*), and 473 K (*3*).

The kinetic equation of the reaction (9) based on the proposed Scheme 1 satisfactorily describes the experimental data. Therefore, it can be concluded that the surface disproportionation of the hydroxyls

$$2\ OH_{ads} = H_2O + O_{ads} + \square \qquad (VI)$$

does not substantially contribute to the occurrence of the reaction. Under the studied conditions, the stationary reaction proceeds *via* the hydrogenation of the surface hydroxyls.

Based on the study of the interaction of hydrogen with oxygen pre-adsorbed on silver[6] and taking into account the available literature data on disproportionation,[15] it was suggested that this process can proceed *via* two parallel routes: by hydrogenation (III) and by the disproportionation of the surface hydroxyls (VI). However, the results of this work do not indicate that, under the studied conditions, the stationary reaction of hydrogen oxidation proceeds *via* the route including the disproportionation of the surface hydroxyls.

The studies performed gave a detailed account of the effect of the hydrogen to oxygen ratio in the reaction mixture on the rate of hydrogen oxidation on silver.

The data of previous works on separate analysis of the kinetics of the interaction steps suggest that the reaction proceed through the intermediate formation of surface hydroxyls. Taking into account these results, we analyzed the kinetics of the stationary reaction, which made it possible to derive the kinetic reaction equation that satisfactorily describes the experimental data.

To conclude, the adsorbed layer on the silver surface consists predominantly of hydroxyls under the conditions of the stationary reaction.

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